Picosecond Time-Resolved Spectroscopic Study
of
Vibrational Relaxation Processes in Alkali Halides

by

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Vitae

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Abstract

A significant technological advance in the synchronization of a streak camera with a picosecond modelocked laser system has been developed and applied to the first reported study of fluorescence dynamics of impurities in alkali halides with picosecond time resolution. The vibrational dynamics of fluorescent impurities such as color centers, metal ions and molecular ions are investigated through techniques of time-resolved spectroscopy with a jitter-free signal averaging streak camera system developed in this thesis. This study has yielded valuable new information about vibrational relaxation processes which govern the fluorescence properties of defects at short times after excitation with a picosecond optical pulse. In this thesis the first systematic study of fluorescence dynamics in the limits of strong and weak impurity-lattice coupling is presented. The time-resolved fluorescence spectrum of a vibrationally relaxing molecular ion in several alkali halide hosts is directly measured for the first time. Hot luminescence lines are detected at short times after excitation revealing details about the excited states of the molecular ion. Existing theories of multilevel vibrational relaxation and multiphonon relaxation are

investigated. Several important conclusions about the impurity-lattice coupling mechanism are made.

Operation and design principles and applications of the jitter-free streak camera system are discussed. Several suggestions for further system improvements are offered.

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CHAPTER 1 INTRODUCTION

1.1 Vibrational Relaxation of Defects

In the optical excitation of isolated atoms linewidths in the 100 MHz range for fluorescence and absorption transitions are common. One major difference in the absorption and fluorescence spectra of color centers is the great breadth of the lines (0.2 eV typically or 50 THz). The reason for this is that the excited states of the isolated atom can decay only by radiative emission, a relatively slow process, whereas when the atom is inserted into a solid its excited states can decay much more rapidly by emission of phonons or a variety of other processes which are impossible in the case of an isolated atom. As a consequence of the short lifetimes of the states the energies are poorly defined and broad transitions result. Collisional line broadening in atomic vapor systems is somewhat analogous to line broadening of impurity energy levels in condensed media however in a typical dilute gas of 10^{10} to 10^{13} atoms per cm^3 the collisional linewidth is only about 10 MHz. Thus the color center can be viewed as a simple atomic system connected via a complicated interaction to a large energy sink, or a heat bath.

Metal ions with s^2 outermost electron configuration such as Tl^+ and Pb^+ are impurities which are strongly coupled to the lattice as in the case of the F center. Another class of fluorescent impurities is the molecular ion such as O_2^- , S_2^- , Se_2^- , etc. These negative paramagnetic molecular ions form an extremely interesting class of study because they act as local probes of the lattice dynamics. This is the case because they have a well-defined vibrational structure of their own which is only weakly perturbed by the crystal environment. Their small size is one reason for this. For O_2^- the excited state wavefunction is small ($1.3 \text{ \AA}$) compared to the lattice constant of the host ($3-5 \text{ \AA}$). Another reason is that their intramolecular vibration frequency ($300-1000 \text{ cm}^{-1}$) is high compared to the lattice phonon frequencies ($100-200 \text{ cm}^{-1}$). Both of these factors contribute to a reduced coupling strength of the molecular ions in alkali halides compared to the case of color centers and s^2 metal ions. Another important feature about the study of molecular ion impurities is that they represent an attractive case for theoretical study where the impurity is strongly electrostatically coupled to the lattice but weakly vibrationally coupled.

Rare-earth impurities such as Nd^{3+} exhibit primarily a zero-phonon line with very small multiphonon sidebands. In this case the coupling is primarily of high multiphonon

order and the electronic wavefunctions are again small compared to the lattice constant. This case is intermediate between the isolated atom and the molecular ion in coupling-induced broadening of the spectrum.

The optical excitation cycle of an impurity coupled to an alkali halide lattice is conveniently represented in terms of a configuration coordinate diagram of the type used to describe molecular energy levels. Many of the qualitative features of impurity-lattice coupling can be visualized using such a diagram (Fowler and Dexter 1965) (Figure 1.1). Optical excitation causes an "instantaneous" (i.e. in the femtosecond range) transition from $|g,0\rangle$ to $|e,n\rangle$. This transition is represented by a vertical line "A" in the diagram because the electronic state can change in a time which is short compared to the crystal phonon period (300 fs). An isolated atom would then emit from this state, but a coupled atom can transfer energy to the host (heat bath) via phonon emission until a metastable point (the electrostatic equilibrium point) is reached: $|e,0\rangle$. At this point the lattice is distorted to a new position R_0 by the electrostatic interaction of the excited state wavefunction with the lattice and the center undergoes a photon emission process "E" whereby the state changes to $|g,m\rangle$. A further phonon emission in the ground state then returns the center to $|g,0\rangle$. The properties of the

Figure 1.1 Configuration coordinate diagram of color center.

emitted fluorescence photon will depend on the initial state of the center $|e,n\rangle$ at the instant of the transition in a direct manner. Thus the vibrational state (or states) of the center can be investigated by studying the fluorescence properties of the center. In particular if the time course of the fluorescence is followed with sufficient time resolution the vibrational state of the center $\langle n(t) \rangle$ may be determined. The rate at which $\langle n(t) \rangle$ changes will be related to the details of the impurity center and local environment and the rate at which $\langle n(t) \rangle$ relaxes will be referred to as the vibrational relaxation rate, or VR rate, of the center. This picture predicts the occurrence of "hot" luminescence lines, or fluorescence which is emitted at a higher energy than that which is emitted from the metastable point $|e,0\rangle$. Such a transition is denoted by "h" in Figure 1.1. The measurement of hot luminescence gives direct information about the excited state vibrational dynamics. In the case of impurities which are coupled to the lattice weakly enough to permit the observation of vibronic details in the spectrum, the kinetics of several individual vibrational levels may be measured simultaneously.

1.2 Literature Review

The process of vibrational relaxation has been studied extensively both experimentally and theoretically in a wide variety of media. Freed (1976) has reviewed studies of VR in relation to electronic processes. Experimental studies of vibrational relaxation (VR) have been performed in gases, rare gas matrices, molecular beams, liquids and solids. The rate of relaxation of vibrational energy covers a very large range in these systems, from about one second to less than one picosecond (10^{-12} s). In the case of relaxation of impurity molecules in condensed media VR times in the picosecond range are common. A fuller understanding of the basic mechanisms involved in VR processes is required. Scaling laws describing the variation of VR rates with such parameters as temperature, host properties and wavelength are needed for a better understanding of the VR process particularly in short time scales. These results will have application in theories of energy transfer, laser physics, molecular physics and chemistry.

The case of VR of an impurity molecule in a solid is of particular importance in theory of laser operation. Color centers in alkali halides (Fowler 1968a) have been used to generate picosecond laser pulses of wide tunability in the near infrared (Mollenauer and Bloom 1979). A new class of thallium-stabilized centers shows great promise as a stable near infrared color center laser

(Gellermann et al. 1982). In this class the VR rates have been thought to be greater than 10^{11} s^{-1} , as a strong electron-phonon coupling in ionic crystals is expected to lead to large VR rates for color centers. A class of laser materials which have known since the mid-1960s is being rediscovered: the vibronic laser. Using the Cr^{3+} ion in chrysoberyl (Alexandrite) and in beryllium aluminum silicate (Emerald) lasing on the vibronic sidebands of the E lines has been demonstrated (Walling and Peterson 1980, Shand and Walling 1982). The vibrational details of the lasing transitions are poorly understood. Recently vibrational fluorescence has been observed from F center - CN^- ion complexes (Yang and Luty 1983). This has the potential to create a totally new class of infrared laser materials. Again, a deeper understanding of the VR process in ionic crystals is required.

Several optical techniques are available for studying VR in condensed media with picosecond time resolution. These are Raman scattering, pump-probe spectroscopy and fluorescence spectroscopy. Raman scattering experiments address the instantaneous vibrational population with a time resolution given by the pump and probe pulse durations. Continuous wave (CW) measurements of Raman spectra of color centers have been made (Warlock and Porto 1965), but time-resolved Raman scattering techniques have not been applied to a study of color centers. The

lifetime of optical phonons in CaF_2 was measured by Alfano and Shapiro (1971) using a time-resolved Raman scattering technique.

Measurements of VR of F centers in KCl were made by Belke et al. (1981) using a pump-probe technique to measure the gain induced by an intense pump beam. It was not possible to resolve the risetime and a risetime of less than 10 ps was inferred. Using a subpicosecond pulse dye laser system (0.7 ps FWHM) simultaneously pumping a color center laser at 2.61 μm , Wiesenfeld et al. (1981) measured the onset time for gain of F_A centers in $\text{KCl}:\text{Li}$. A risetime in the range of 1-13 ps was found with a temperature dependence characteristic of a multiphonon process. Akhmanov et al. (1982) used a pump-probe technique to measure the absorption kinetics of F centers in KBr. A relaxation time of around 10 ps was inferred. The gain kinetics of F_2 centers (M centers) in LiF were measured by Bruckner et al. (1983) using 10 ps pulses. Risetime of less than 10 ps was inferred by comparison with rhodamine 6G dye. The fluorescence risetime of R6G dye was investigated with a Kerr gate technique by Mourou and Malley (1975) and found to be less than 2 ps.

Despite all this activity there have been no direct measurements of the dynamics of fluorescence of color centers with picosecond time resolution to date. The fluorescence intensity has a simple and direct

relationship to the excited state population and offers new information about the VR process. Since the technique does not rely on the inducement of substantial population modulation as in the case of pump and probe gain measurements, it is in general a small-signal technique. In some pump-probe experiments up to 80% of the ground state population may be depleted. This undoubtedly results in additional effects which are not directly related to the VR process.

Some information about VR of molecular ions has been inferred from CW spectroscopic studies of fluorescence using a photon-counting technique (Saari 1971). Rates of VR have been estimated in the range of 2 to 50 ps. Since this technique is not a time-resolving one, many assumptions must be made in order to arrive at these estimates. Also since the technique relies on the individual identification and assignment of spectral lines, it cannot be used to study systems with fast relaxation in which little spectral structure is observed.

1.3 Experimental Techniques

Direct recording of fluorescence time courses with picosecond resolution can be done with a streak camera (Bradley and Sibbett 1975 and Fleming et al. 1977) however a standard streak camera is not capable of achieving sufficient signal to noise ratio to make the detailed measurements which are reported here. In this

work a novel method of streak camera deflection is invented which offers the capability of extensive signal averaging. The development of this streak camera system and its application to the study of VR of fluorescent defects in alkali halide crystals comprise this thesis. The system is described in detail in Appendix I.

1.4 Outline

The objective of this thesis is to study VR of certain color centers, molecular ions, and metal ions in alkali halide crystals using techniques of picosecond fluorescence spectroscopy with a jitter-free signal averaging streak camera system. In Chapter 2 the experimental results are presented. The variation of the fluorescence kinetics with defect species, host crystal, temperature and polarization is experimentally investigated. Experimental factors dictated which impurity centers could be studied on the picosecond time scale using the techniques developed here. In each impurity class studied one or several centers were selected. In particular the following centers were studied: M centers in NaF and LiF, O_2^- in several hosts, S_2^- in KI and Tl^+ in KBr. The time-resolved fluorescence spectrum of a molecular ion undergoing VR is directly measured for the first time.

In Chapter 3 the theoretical interpretation of the experimental results is given. The theoretical problem of describing the VR of an impurity in an alkali halide matrix has not been solved in any detail at this time and it is not altogether clear whether existing theories of VR in condensed media can be directly applied to an understanding of the results obtained here. Therefore, the theoretical discussion is limited to estimating VR rates in various crystals and applying existing models of multilevel dynamics to the spectrum calculation. One simple harmonic model of the VR of a molecular ion in alkali halide crystals is developed to estimate the absolute VR rate in a simple way. It is found that using data from the literature on Raman scattering and low frequency dielectric constant measurements the absolute rates of VR can be estimated. These values are found to agree favorably with the experimentally observed results. Although this model is trivial compared to the sophisticated theories of VR which have been developed, it has a certain validity for the case of molecular ions in alkali halides where the VR times are roughly 1000 times longer than the vibration period of the ion. In this situation a harmonic model may be expected to be valid. The particular importance of this simple model is that no other theory has been developed which is capable of estimating absolute VR rates in alkali halide crystals.

Information about the local mode relaxation time can be obtained from this model in a straight forward way.

A model for the excited states of O_2 is proposed which is consistent with existing knowledge and the new results which have been obtained here. A model of multiphonon relaxation rates is investigated. Some important conclusions about the VR mechanism are drawn.

Chapter 4 concludes the discussion and offers suggestions for further improvements in experimental techniques. Appendix I contains a discussion of the experimental considerations involved in picosecond time resolved fluorescence measurements and a detailed discussion of the jitter-free streak camera system. Appendix II contains a discussion of sample preparation procedures, laser system parameters and some considerations for absolute picosecond fluorescence timing measurements.

CHAPTER 2 EXPERIMENTAL RESULTS

2.1 Optical Lineshapes

The starting point for this work is the measurement of optical lineshapes of the impurities of interest here. Centers which are of interest here are those which satisfy certain criteria for picosecond fluorescence detection. First, the center must exhibit an absorption (excitation) peak in a wavelength region which can be accessed with the modelocked laser system (Appendix II). Second, the fluorescence must occur within the range of detection sensitivity of the streak camera (Appendix I). Third, the fluorescence decay time must not be too long, and fourth the concentration of the species must be sufficient.

Since all the results of CW spectroscopy presented here have been previously shown by many authors, the measurement of these spectra serves as a check of the validity of the spectroscopic assignments of picosecond fluorescence signals and sample preparation procedures. In the case of picosecond excitation it was verified that the same emission spectrum (time-integrated) results as in the case of CW excitation. This serves as additional assurance that the signals presented here indeed represent the desired fluorescent species.

2.1.1 Absorption Spectra

The absorption spectrum at 300°K of a LiF crystal after gamma-ray irradiation for several hours is shown in Figure 2.1a. Absorption peaks appear at wavelengths corresponding to F, M and R centers. Even at 0°K no structure is observed in the F or M absorption bands. The R₂ band in LiF shows some structure at low temperature (Fowler 1968a). In LiF the F center has no emission (Bartram and Stoneham 1975) because of direct nonradiative deactivation to the ground state via a curve crossing mechanism but the M center shows a strong emission at about 700 nm. . The M center picosecond fluorescence dynamics were studied using excitation at 467 nm, as indicated by the vertical line in Figure 2.1a.

The absorption of a 1 mm thick crystal of KBr:O₂ at 300°K is shown in Figure 2.1b. The rise of absorption at 230 nm may be due to O₂ photoionization or other impurities such as OH⁻. The primary fluorescence is excited in the region of 280 nm. A weak shoulder is observed at about this wavelength in Figure 2.1b. The O₂ center was excited by the fourth harmonic of the Nd³⁺:YAG at 266 nm, as indicated in Figure 2.1b.

The absorption spectrum at 300 °K of a 2 mm thick crystal of KBr:Tl⁺ is shown in Figure 2.1c. The familiar "A", "B" and "C" absorption bands are clearly shown. Excitation into the "A" band produces the simplest fluorescence emission spectrum (Edgerton and Teegarden

Figure 2.1 Absorption spectra of (a) gamma-irradiated LiF, (b) pure KBr and KBr:O₂⁻ and (c) KBr:Tl⁺ at 300 °K. Vertical lines denote excitation wavelengths used in picosecond time-resolved fluorescence studies.

1964). In KBr the "A" band is efficiently excited by the fourth harmonic at 266 nm, as indicated in Figure 2.1c.

2.1.2 Emission Spectra

It is well known that the emission spectra of color centers such as F and M centers exhibit little vibrational structure. In Figure 2.2a part of the fluorescence spectrum of the M center in NaF is shown with excitation at 460 nm. The measurement resolution was 1.3 nm. It is clear that the emission is completely unstructured even at 20°K. On the other hand the emission spectrum of O_2^- in alkali halide crystals shows sharp structure. In Figure 2.2b the fluorescence spectrum of KBr: O_2^- at 20°K is shown. The existence of sharp structure which is repeated in the various lines throughout the spectrum is in excellent agreement with previous measurements (Ikezawa and Rolfe 1973, Rebane and Rebane 1974). This structure is representative of the vibrational mode of oscillation of the O_2^- molecule at about 1000 cm^{-1} . The individual sidebands are due to the multiphonon interaction the details of which depend on the particular host crystal (Rolfe et al. 1973). The spectrum measured with excitation from the 254 nm mercury line is identical to the spectrum measured with excitation from a 20 ps laser pulse. This indicates the validity of using picosecond excitation at 266 nm to address the same optical states of

Figure 2.2. Fluorescence spectra of (a) M center in NaF and (b) KBr:O₂ at 20 °K.

O_2 as in the case of CW excitation which has been used in previous studies.

The fluorescence spectrum of the Tl^+ in KBr was not measured here because of the lack of response of the OMA to UV radiation of wavelengths less than 360 nm but it is known to contain broad unstructured bands (Edgerton and Teegarden 1964).

2.1.3 Excitation Spectra

Measurements of the absorption spectra of impurities in alkali halides fail to show unambiguously the presence of certain fluorescent species. This is in part due to the absorption from other nonfluorescent species which are introduced during the doping process and in part due to the low concentrations which are typically obtained. In the case of O_2 other centers may be formed such as O_3 and higher order aggregate centers. In such a case the excitation spectrum yields more reliable information about the origin of the fluorescence. The excitation spectrum of O_2 in KBr at 300°K is shown in Figure 2.3. Excitation at 266 nm matches quite well with the O_2 excitation band. At low temperature (2°K) a weak periodic structure was found in the excitation spectrum of O_2 in KBr using a high resolution spectroscopic technique (Ikezawa and Rolfe 1973). Superimposed on a broad background, the weak structure rapidly vanishes as the vibrational quantum number exceeds about five. The structure indicates a

Figure 2.3 Excitation spectrum of 577 nm fluorescence of KBr:O₂ at 300 °K.

vibrational frequency of 575 cm^{-1} in the excited electronic state.

2.1.4 Temperature Effects

The effect of temperature on the sharp vibronic lines has been studied extensively both experimentally and theoretically. At very low temperature the width of the zero phonon lines in the spectrum of KBr:O_2 scales with the square of the temperature in the range of 4 to 30°K (Rebane and Rebane 1974). At low temperatures the quadratic dependence is believed to be due to the interaction of the impurity with pseudolocal low frequency modes. The fluorescence spectra of KBr:O_2 measured at room temperature and low temperature are shown in Figure 2.4a and 2.4b, respectively. At 300°K the vibrational structure persists.

The temperature dependence of the relative quantum efficiency of O_2 in the three crystals KCl , KBr and KI is shown in Figure 2.5. The fluorescence of O_2 persists even at room temperature because the energy of nonradiative deactivation corresponds to about 1000°K . This compares with a nonradiative deactivation temperature of about 150°K for color centers. For KI the situation is a bit different. These measurements agree well with previously published results (Rebane 1972).

Figure 2.4 Fluorescence spectrum of $\text{KBr}:\text{O}_2$ at (a) 300 $^{\circ}\text{K}$ and (b) 20 $^{\circ}\text{K}$ with CW excitation at 254 nm.

2.1.5 Summary of Lineshape Measurements

These results may be summarized as follows. The three cases of impurity considered here fall into two categories: strong coupling and weak coupling. For the case of color centers (M centers in NaF and LiF) and s^2 metal ions (Tl^+) the absence of structure in the absorption and fluorescence spectra indicates strong coupling of the impurity and the lattice. For the case of molecular ions (O_2^-) the appearance of sharp structure implies a weaker coupling of the impurity to the lattice. In this thesis the direct connection between the experimentally measured VR rate and the coupling strength of these classes of impurities is shown.

2.2 Fluorescence Risetime Measurements

2.2.1 Introduction

The VR process of a defect in alkali halides may not be well described by a simple one dimensional configuration coordinate diagram such as Figure 1.1. The fluorescence response to an ultrashort excitation pulse is probably an extremely complicated function, the form of which depends critically upon the details of the electronic wavefunction and localized lattice configuration about which little or nothing is known. In any case in order to get started in measuring the VR rates of defects in alkali halides a very simple model is adopted which characterizes all the dynamics of the VR

Figure 2.5 Temperature dependence of the fluorescence quantum efficiency of O_2 in (a) KCl (b) KBr and (c) KI.

process in a single parameter. In a simplified model of VR (Figure 2.6) the multilevel vibrational manifold is treated as a single vibrational population and the whole system is treated in a three-level approximation. Optical excitation creates a vibrational population in state N_2 . In the simplified model all of the N_2 population decays into the N_1 level with time constant τ . The fluorescent transition proceeds from the N_1 level to the ground state with time constant T . For the purpose of fluorescence dynamics modeling it is not necessary to consider the population dynamics in the ground state.

In order to characterize experimentally the value of the fluorescence response time for a particular center the fluorescence time course of the center and the excitation function are carefully measured for the exact same conditions (Appendix I). Then the excitation function is used to calculate $N_1(t)$. The solution $N_1(t)$ is compared to the measured fluorescence time course. The value of the fluorescence response time τ is then varied and the calculation is repeated until the best fit is obtained. This procedure was implemented at first manually and later using an automatic least-squares optimization routine. In a few cases a two-component fit may provide a slightly more optimal fit but the introduction of the additional parameters serves no useful purpose unless higher signal to noise ratio data can be

Figure 2.6 Three-level approximation to multilevel vibrational relaxation. The level denoted N_2 represents the general vibrational population in the excited state.

obtained to fully separate the individual terms. The result of fitting more complicated multilevel kinetic equations is discussed in Chapter 3.

2.2.2 Scaling of Fluorescence Risetime with Species Color Centers

The general study of VR of color centers in alkali halides by time-resolved fluorescence spectroscopy with a streak camera is greatly restricted by the range of detection sensitivity available. The particular streak camera used in this work was sensitive in the range 190 to 850 nm (Appendix I). There are only a few color centers which fluoresce in the visible range: LiF:M, NaF:M, NaF:F and KF:F. Of these only the two M centers were studied. These serve as prototype centers for the purpose of measurement of characteristic VR rates for color centers. The M center is composed of two electrons trapped at a cation divacancy as opposed to an F center which is composed of an electron trapped at a single cation vacancy. It is reasonable to suppose that the rate of VR of the M center is not drastically different than that of the F center. In Figure 2.7a the fluorescence rise of the M center in NaF at 300°K is shown. A glass filter (OG-590) was used to discriminate against the scattered excitation light at 532 nm. Each trace represents the accumulation of 30 shots. Also shown is the solution to the three level system for $\tau=0, 3$ and 12 ps. The closest

fit is obtained with $\tau=0$ ps, indicating a rapid relaxation. The experimental uncertainty in these curves is ± 1 ps so the risetime in this case is not resolved. At low temperatures the risetime was also observed to be less than 1 ps. This result is consistent with a previous measurement of the gain response of the M center (Bruckner et al. 1983) but instead of a 10 ps uncertainty which was quoted by these authors the uncertainty in these measurements is 1 ps. This is due in part to the high signal-to-noise ratio obtainable with signal averaging and in part to the high stability and reproducibility of the active-passive modelocked Nd³⁺:YAG laser which was constructed and used (Appendix II). The departure of the calculation from the measured fluorescence function for values of $\tau=3$ ps and greater indicates the sensitivity of this technique in measuring response times of less than the excitation pulse width in use (25 ps). A small timing error (-1.5 ps) is indicated for the $\tau=0$ calculation compared to the fluorescence rise. This is due partly to the effects of finite sample thickness and partly to wavelength dependent timing errors. These important effects are discussed in Appendix II.

For the study of VR of the M center in LiF a special experimental setup was required for the generation of the required excitation wavelength of roughly 450 nm. It is difficult to generate blue light with a single-pulse

Figure 2.7 Fluorescence rise of color centers. (a) rise of fluorescence of NaF:M for wavelengths past 590 nm and excitation pulse at 532 nm (30 shot averages), with plots of $N_1(t)$ for $\tau=0, 3$, and 12 ps. (b) rise of fluorescence of LiF:M for wavelengths past 590 nm and excitation pulse at 467 nm (300 shot averages).

X
Nd³⁺:YAG system with only 1 mJ energy. It was found that by using a 10 cm cell of acetone pumped by 30 μ J of 532 nm laser light that both the stokes wave at 615 nm and the antistokes wave at 467 nm could be produced by stimulated Raman scattering (Appendix II). The antistokes wave was collected with a lens which had a central stop to separate the antistokes light from the stokes and residual pump light. In Figure 2.7b the fluorescence rise of the M center in LiF is shown compared to the scattered excitation pulse. The curves represent the summation of 300 shots each. Again the fluorescence rises with a response time of less than 2 ps.

Therefore the fluorescence response of the M center in NaF and LiF is less than 2 ps. At low temperature the risetimes were still too fast to be resolved. In order to discern the behavior of the VR process with respect to several parameters it is necessary to actually resolve and quantify the fluorescence risetime. This would be extremely interesting for the case of color centers but it is not possible to resolve the VR time of color centers using the present methods. Further improvements which should enable the continuation of this study into the subpicosecond regime are discussed in Chapter 4. It is nonetheless important to have shown that the VR time is less than two picoseconds directly since this limit is ten times smaller than the previous experimental limit.

Molecular Ions

The light molecular ions O_2^- and S_2^- when inserted into alkali halides as impurities form luminescence centers with many unique properties. They show a well-resolved vibrational structure and even some librational and rotational structure. They can be considered as a probe for the local lattice dynamics of the host crystal and as an important tool for the study of the electron-phonon interactions. From the point of view of this work they represent an important class of study as a model for VR of an impurity in an alkali halide crystal in the weak coupling limit which should lead to slower VR and fluorescence risetimes which are long enough to be resolved. Of all the molecular ion centers which have been studied the O_2^- and S_2^- centers were the only ones which satisfy the requirements for picosecond fluorescence detection as outlined earlier. Of these the most extensive work was carried out on the O_2^- ion because of several experimental facts. The O_2^- ion has a quantum efficiency of almost unity, it is efficiently excited by the fourth harmonic of Nd^{3+} :YAG which is readily available, the fluorescence emission is completely contained within the optical response of the streak camera, and the fluorescence lifetime is not too long to make picosecond detection impossible (100 ns). In the case of NO_2^- and Se_2^- low quantum efficiency prevented

serious study. A preliminary result for the VR time of the S_2 ion in KI was obtained, but the impossibility of obtaining the correct excitation wavelength precluded serious study of S_2 .

The fluorescence rise of O_2^- in RbI at 20 °K with excitation at 266 nm is shown in Figure 2.8. This measurement represents the fluorescence kinetics for all wavelengths past 590 nm in unpolarized light. Shown in Figure 2.8a is a single shot and in 2.8b a 300 shot summation. With signal averaging in the jitter-free mode it is possible to achieve a much better signal-to-noise ratio than the single shot measurements which are common. In Figure 2.8b the excitation pulse is also shown (its position defines $t=0$) and the result of a least-squares optimized fit to the three level kinetic system with a risetime of 56 ± 5 ps. This result is typical for O_2^- in alkali halides. It should be mentioned that this is the first reported direct measurement of the fluorescence dynamics of the O_2^- ion in alkali halides. The significant value of the jitter-free signal averaging streak camera system is excellently illustrated in this case. In a case such as the O_2^- ion in alkali halides two factors reduce substantially the signal level. First, the fluorescence decay time (100 ns) is much longer than the duration of the measurement (300 ps) so only about 10^{-3} of all the fluorescence which is available in a CW measurement is

Figure 2.8 Rise of fluorescence of RbI:O_2 at 20 °K, (a) one shot and (b) a 300 shot average with excitation at 266 nm and cutoff wavelength of 590 nm. In (b) the fit assuming three level kinetics is displayed. The least-squares optimized fit yields a risetime of 56 ± 5 ps.

emitted in the time scale of the picosecond experiment. Second, the O_2^- ion requires excitation by the fourth harmonic of the laser wherein only a few microjoules of excitation energy is available. These factors combine to produce a weak signal, in the range where the individual photoelectron events from the photocathode begin to register separately. The extensive signal averaging capability of the jitter-free streak camera system can make many experiments possible under extreme conditions which are not possible with conventional streak camera systems.

The fluorescence risetime of the S_2^- ion KI was measured with excitation at 355 nm (the third harmonic of Nd^{3+} :YAG) in a similar manner. In Figure 2.9 the fluorescence rise is shown with a 300 shot summation using a GG475 filter. This measurement was made at 20°K. The poor signal to noise ratio even after a 300 shot summation at high gain is partially due to low S_2^- quantum efficiency and partly to the low efficiency of excitation at 355 nm. At 355 nm the excitation spectrum of S_2^- shows a minimum (Rebane and Rebane 1974) and it was not possible to generate the 400 nm light required for better excitation. Also shown is the three level fit for $\tau=0$ and $\tau=30$ ps. The risetime appears to be in the range of 30 to 40 ps. At room temperature there was no measurable fluorescence.

Figure 2.9 Rise of fluorescence of S_2 in KI at 20 °K with excitation at 355 nm and detection cutoff of 475 nm (300 shot averages). Also shown are the three level kinetic solutions for $\tau = 0$ and $\tau = 30$ ps. Poor signal to noise ratio results from low quantum efficiency and low efficiency of excitation at 355 nm.

s² Metal Ions

The situation is quite different for metal ions in alkali halides. In the case of a heavy metal ion such as Tl⁺ or Pb⁺ the local mode of vibration is likely to consist of the nearest neighbor lattice ions vibrating with respect to the heavy impurity. In the case of the light molecular ion impurity such as O₂ the vibration is intramolecular and relatively free with respect to the lattice. For Tl⁺ the local mode resonance is at about 70 cm⁻¹, or about half of the typical lattice frequency. In this case rapid VR is expected since the low frequency mode can directly couple to the acoustic phonon modes.

Of all the possible metal ions for study in this class only KBr:Tl⁺ and Cr³⁺ in chrysoberyl (Alexandrite) were studied. Of these, results were obtained only for the Tl⁺ ion in KBr. The thallium center has been studied theoretically (Knox 1967) and experimentally (Fowler 1968b). One feature of the Tl⁺ center is the long fluorescence lifetime components. The amount of signal available for detection on the picosecond time scale decreases as the lifetime increases because the radiative rate decreases. This long lifetime is equivalent to the retrace time of the jitter-free streak camera (100 μs). Therefore a special differential technique was required to extract the picosecond information from the long retracing background. Figure 2.10 shows the time resolved

Figure 2.10 Fluorescence rise of Tl^+ in KBr at 20 °K.

X fluorescence of ~~for~~ KBr:Tl⁺ excited at 266 nm at 20°K using a pair of blocking filters (WG305 and UG-11) which give a transmission window from 305 to 390 nm.

In Figure 2.10a fluorescence measurements are shown for two settings of the optical delay line: 0 and 200 ps. The background which rises toward early times is from the long lifetime fluorescence component of the emission during the retracing of the streak camera (Appendix I). Taking the difference of the two curves in Figure 2.10a and considering only the rising portion, Figure 2.10b shows the rise of emission of the Tl⁺ center compensated for the retracing background. These data represent the summation of 300 shots each. The fluorescence rises with a response time of less than a few ps, so the VR time of this center is less than a few ps.

A similar experiment was performed on Alexandrite, an important new vibronic laser material which consists of Cr³⁺ in chrysoberyl. It was not possible to observe any picosecond modulation of the long time background in this case, however. The fluorescence lifetime of this emission was about 400 μ s at room temperature. With a single exponential decay of 400 μ s one does not expect to be able to detect the modulation due to the signal during the first few hundred picoseconds, since there would be 10⁶ times less signal in the fast component than in the retracing background. The differential technique requires

at least a 1% modulation to enable detection with 300 shot averages. For the case of Tl^+ in KBr there must be an additional fast (10-100 ns) but weak component to the decay following the initial VR of the center which was not resolved in previous measurements. The emission of Tl^+ in KI exhibits a fast (10 ns) decay and a slow (10 μ s) decay (Fowler 1968c). It is quite plausible that KBr: Tl^+ also exhibits a fast decay.

2.2.3 Scaling of Fluorescence Risetime with Host

Detailed measurements of fluorescence risetimes were thus only possible for the O_2^- ion in alkali halides since the fluorescence risetimes of other centers were unresolvable (less than a few ps). With the capability to make accurate measurements of the fluorescence risetimes of the O_2^- ion certain simple experiments can be performed which may elucidate the mechanism of VR. One such experiment would be to insert the O_2^- ion into various crystals and measure the fluorescence risetime as a function of the host properties. It was possible to grow and dope samples of KBr: O_2^- , KCl: O_2^- , KI: O_2^- , NaCl: O_2^- and RbI: O_2^- . The NaCl crystal showed a weak O_2^- fluorescence and a strong broad blue emission of unknown origin. This interfered with the measurement of the fluorescence kinetics. The blue emission is probably from the O_2^- ion but it could be related to the host. The KI crystal

Figure 2.11 Fluorescence rise of O_2 in (a) KCl, (b) KBr and (c) RbI at 20 °K with excitation at 266 nm and detection cutoff of 645 nm (300 shot averages). Least-squares optimized three level kinetic fits are shown.

exhibited a weak signal so detailed studies were not performed.

The fluorescence rise of O_2 in KCl, KBr and RbI is shown in Figure 2.11. These data are all taken with an RG645 cutoff filter passing light beyond 645 nm. The reason for this procedure is discussed in the next section. A definite effect of the host crystal on the fluorescence risetime is revealed. The three level optimized fits yield the following values for the relaxation times : $\tau_{KCl} = 15 \pm 4$ ps, $\tau_{KBr} = 41 \pm 6$ ps and $\tau_{RbI} = 79 \pm 11$ ps.

2.2.4 Scaling of the Fluorescence Risetime with Cutoff Energy

The time course measured in this energy-integrated manner represents the kinetics of all the emission at wavelengths longer than a cutoff wavelength dictated by the glass filter in use. The low energy or long wavelength cutoff is determined by the streak camera optical response. Using a set of glass filters with cutoff wavelength in the range 305 nm to 695 nm the fluorescence rise function of O_2 in several crystals was measured. In Figure 2.12 a typical result is displayed. For RbI: O_2 at 20°K the fluorescence rise is shown for (a) cut at 395 nm, and (b) cut at 590 nm. The three-level optimized fits yield risetimes of $\tau = 8 \pm 2$ ps and $\tau = 60 \pm 8$ ps, respectively. The trend toward shorter risetimes

with decreasing cutoff wavelength is exhibited by O_2 in all alkali halides investigated. In order to characterize the dependence of the risetime with cutoff energy the fluorescence rise was measured over the entire range of cutoff wavelengths available and in each case an optimized fit was obtained. The results are plotted as inverse risetime, or rise rate versus the energy corresponding to the cutoff wavelength. In Figure 2.13 the rise rate distributions for (a) KCl, (b) KBr and (c) RbI are shown. For KCl and KBr a sharp break point at about 2.6 eV is indicated above which the rise rate rapidly increases. RbI does not exhibit such a sharp break point.

This complex behavior is related to the blue emission which was previously discussed. For a fuller understanding of this the results of the time-resolved spectroscopy at the UV end are required. These are discussed in Section 2.3. For the case of KBr and KCl the rise rate appears to approach a constant value at the limit of cutoff energy below about 1.5 eV. In the long wavelength limit no hot luminescence components are detected since they occur at higher energy. In addition the fast rising blue emission is rejected.

2.2.5. Scaling of Fluorescence Risetime with Temperature

Figure 2.12 Fluorescence rise of O_2 in RbI at 20 °K with detection cutoff of (a) 395 nm and (b) 590 nm with fits of $\tau = 8 \pm 2$ ps and $\tau = 60 \pm 8$ ps, respectively.

Figure 2.13 Rise rate distributions of O_2 in (a) KBr, (b) KCl and (c) RbI at 20 °K.

The temperature dependence of the VR rate is a quantity of interest in studies of VR of impurities in condensed media. In Figure 2.14 the fluorescence risetime of KBr:O_2^- is shown at (a) 20 °K and (b) 300 °K. The fits give risetimes of 34 ± 4 ps and 39 ± 4 ps, respectively. Within experimental error the rate of VR is thus independent of temperature over this range. It should be noted that the VR rate is effectively constant even though the CW fluorescence spectrum changes dramatically over this temperature range (Figure 2.4).

2.2.6 Summary of Risetime Measurements

To summarize the results of the risetime measurements, it was found that for M centers and Tl^+ the fluorescence rises with a response time of less than a few ps. For the case of the molecular ions O_2^- and S_2^- risetimes of about 50 ps were measured. The scaling of the fluorescence risetime of O_2^- with host was investigated for several crystals and risetimes in the range of 15 to 80 ps were measured. The dependence of the fluorescence risetime with temperature was investigated. Little or no variation was observed in the VR rate over a wide temperature range. The scaling of the risetime with detection cutoff energy was quantified by obtaining least squares optimized fits of a three level model to the data for each cutoff wavelength in the range 305 to 695 nm.

Figure 2.14 Fluorescence rise of O_2^- in KBr at (a) 20 °K and (b) 300 °K with detection cutoff of 590 nm (300 shot averages). Fits yield risetimes of 34 ± 4 ps and 39 ± 4 ps, respectively.

2.3 Time Resolved Spectroscopy

2.3.1 Introduction

The measurement of the time development of a fluorescence spectrum with picosecond resolution is a difficult task. The streak camera is well suited to this measurement in principle but in practice the problem of jitter and subsequent lack of signal averaging capability makes the data obtained useless. The need to use fully two-dimensional data acquisition in order to acquire all the time and spectral information simultaneously in one shot puts additional practical constraints on the technique when implemented in a conventional fashion.

The jitter-free streak camera (Appendix I) is much better suited to the problem of time resolved spectroscopy because of its extensive signal averaging capability and absolute timing stability. Excellent results have been obtained for O_2 in KBr. Time resolved spectra have been acquired with 25 ps time resolution and 3 nm spectral resolution. The kinetics of the zero phonon lines and hot luminescence components have been separately measured. Several important conclusions about the VR dynamics are made. The experimental setup and details for this measurement are discussed in Appendix I.

2.3.2 Experimental Results for KBr: O_2

Visible

A measurement of the time-resolved fluorescence spectrum of O_2 in KBr is shown in Figure 2.15. Each curve represents the fluorescence spectrum gated for 25 picoseconds (the time interval is set equal to the excitation pulsewidth) with an accumulation of 100 shots per time setting. The result is a clear indication of hot luminescence lines which exist at short times after excitation. The position of $t=0$ is defined as the position of the excitation pulse. The smooth lines are drawn to emphasize the time courses of certain spectral features. The three rising curves follow the time development of the three ordinary lines I_{07} , I_{08} and I_{09} , where I_{nm} denotes the vibronic transition $|e,n\rangle$ to $|g,m\rangle$. The most clearly resolved hot luminescence feature occurs at time $t=17$ ps in the spectral range between I_{07} and I_{08} . This feature, identified as I_{18} decays into the multiphonon sideband of line I_{07} . Another way to view this data is shown in Figure 2.16a where the time-resolved spectra are plotted in a normalized fashion for several selected times. In both of these figures the spectral calibration and resolution is shown on the energy axis. This is a recording of the scattered second harmonic pulse (532 nm) taken in the same configuration as the fluorescence is collected. In Figure 2.16a the spectrum at time $t=0$ is composed of several complex

Figure 2.15 Time resolved spectrum of O_2^- in KBr.

structures. By comparison with the time-integrated spectrum the features I_{07} , I_{08} and I_{09} can be distinguished. The additional features at 17 and 33 ps which are clearly separated from the lines I_{08} and I_{09} can be identified as hot luminescence lines I_{18} and I_{19} . The scheme for the identification of hot luminescence lines is shown in Figure 2.16b. The time-dependence of the intensities of these features gives a direct measure of the vibrational dynamics in the excited state manifold. According to the scheme in Figure 2.16b the hot luminescence features I_{18} and I_{19} should appear at an energy of ω_e higher than the corresponding ordinary luminescence lines and the further lines I_{29} and $I_{2.10}$ should appear at an energy which is $2\omega_e$ shifted. The positions of the identified spectral features are consistent with an excited state vibrational frequency of about 650 cm^{-1} . The value quoted in the literature for KBr:O_2 is 575 cm^{-1} . This is not a serious disagreement for reasons which will be discussed. The spectral features identified as I_{29} and $I_{2.10}$ exhibit a different lineshape than the $n=1$ components. At time $t=0$ the features appear to have a rectangular shape which could be an indication of an underlying series of unresolved structures. A greater width of the hot luminescence lines as the vibrational quantum number increases could be an indication of a rapidly increasing VR rate. This could

Figure 2.16 (a) Normalized time-resolved spectra of O_2 in KBr at 20 °K at several selected times, and (b) scheme for identification of hot luminescence lines.

result from increased coupling of the manifold as the vibrational quantum number increases. The $n=2$ features decay much more rapidly than the $n=1$ features. This would be consistent with increased coupling in the higher vibrational levels in the electronic excited state. In Figure 2.17 the time courses of several of the identified spectral features are plotted from these measurements. The peak intensity of the ordinary feature I_{08} at time t is directly plotted. The intensities of the hot lines I_{18} and I_{29} are estimated by subtracting the value of the multiphonon sideband of line I_{08} in the spectral region of each line. The time courses of the individual lines can then be compared to multilevel relaxation theory.

It is not possible at this point to identify features corresponding to transitions with n greater than 2. One possible reason for this is that the rate constant for VR increases very rapidly with the vibrational quantum number n , as mentioned before. This effect would reduce significantly the intensities of the higher components.

The time course within any specific energy region can be directly measured with this technique by simply rotating the OMA image detector by 90° so that the linescan is parallel to the time axis as in all the previous measurements. By selecting the scan region and the width of the scan of the OMA the time dependence within any spectral region can be directly measured. In

Figure 2.17 Time dependence of hot and ordinary lines in the time resolved fluorescence spectrum of Figure 2.15. (a) Approximate position and shape of excitation pulse, (b) rise of the ordinary line I_{08} , (c) rise and decay of the hot line I_{19} and (d) rise and decay of the hot line $I_{2.10}$.

Figure 2.18 the result of this is shown for the same experimental conditions as in Figures 2.15-17. Figure 2.18a shows the time dependence of the single line I_{08} . Moving the measurement window to a point halfway inbetween the I_{08} and I_{09} lines the signal (b) is recorded. This signal is quite different than (a), with a fast rise followed by a decay to a non-zero value. This is consistent with the time-resolved spectrum measurements since the hot lines occur on the multiphonon sidebands of the ordinary lines, as mentioned previously. These data are fit to (a) the three-level rise of $N_1(t)$ with a risetime of 30 ps and (b) the three-level $N_2(t)$ solution plus a fraction of $N_1(t)$ to allow for the multiphonon contribution. In this case adding 14% of $N_1(t)$ is found to give a good fit. Thus the kinetics of individual features in the time-resolved spectrum can be directly measured. In this case poor signal-to-noise ratio is obtained even after 300 shot accumulations because very little signal is contained in the single lines of the spectrum.

Thus the time-resolved spectrum measurement gives direct evidence that hot luminescence components exist for a short time after excitation and have approximately the same decay time as the risetime of the ordinary component.

Figure 2.18 Direct measurement of hot luminescence of O_2 in KBr with detection parallel to time axis. (a) Line I_{08} and 8(b) detection between I_{08} and I_{09} .

Ultraviolet

The result at the ultraviolet end is not as simple as in the visible. One significant limitation was encountered in this particular experiment. The diffraction grating which was used in these experiments was blazed for 500 nm. Below this wavelength the efficiency drops rapidly. In Figure 2.19 the time resolved spectrum of KBr:O_2^- at the ultraviolet end is shown. The spectral calibration is approximate. A rapidly rising broadband fluorescence signal is indicated. It moves rapidly to the blue end and then the line structure characteristic of the O_2^- ion appears with the usual risetime. There are no additional sharp UV lines at short times which would result from very hot transitions.

2.3.4 Experimental Results for KCl:O_2^-

Figure 2.20 shows the time-resolved spectrum of KCl:O_2^- . The situation is quite different than for KBr . First, the time-integrated spectrum shows twice as many components as the KBr:O_2^- (all scales are the same for the time-resolved spectra). This is attributed to a splitting of the ground state of -525 cm^{-1} (Rebane 1973). The width of the multiphonon sidebands is greater for KCl than for KBr because of the increased coupling strength (Rolfe et al. 1973). The zero-phonon lines are not observed in this measurement because either the temperature was not low enough or the resolution was not great enough. The

Figure 2.19 UV time-resolved fluorescence spectrum of O_2 in KBr at 20 °K. A rapidly rising broadband UV component is detected.

rise of the bands is faster in KCl than in KBr in agreement with the cutoff filter measurements (Figure 2.11). No hot components are observed at short times. This could be due to extremely rapid relaxation and/or small Franck-Condon factors. The two sets of lines rise with roughly the same kinetics, which is consistent with the idea that they represent transitions from the lowest vibrational level in the electronic excited state $|e,0\rangle$ to the vibrational levels in the two ground states $|g1,m\rangle$ and $|g2,m\rangle$.

2.3.5 Summary

The measurement of the time resolved spectrum yields a large amount of information about the VR process. In particular, information about the time development of the multiphonon sidebands, number, shape and position of the hot luminescence components and the UV spectral kinetics has been obtained. Some important conclusions can be made based upon these measurements. From a technological point of view the measurement of time-resolved spectra in the case of a long fluorescence lifetime (100 ns) with this accuracy has never before been done. The spectral resolution of 3 nm was close to the limit which can be theoretically obtained while maintaining a 25 ps time resolution with a single grating system. The VR rate measured by the time resolved spectroscopy technique agrees well with that measured by the cutoff filter

Figure 2.20 Time resolved fluorescence spectrum of O₂⁻ in KCl at 20 °K. All conditions the same as in Figure 2.15 for KBr:O₂⁻.

technique in the long wavelength limit. The jitter-free streak camera system was used to full advantage in this experiment.

2.4 Polarization of Fluorescence

2.4.1 Introduction

The fluorescence polarization contains information about the orientation of the dipole moment of the electronic transition at the instant of the fluorescence transition. It is widely used on a CW basis in chemistry and biology as a probe for rotational motions (Yguerabide 1972). The time development of the fluorescence polarization should be a quantity of interest in the study of VR processes. It has been proposed that the VR process itself causes a depolarization of the fluorescence. This is suggested as the reason that F-centers and molecular ions emit totally depolarized light. It is nonetheless possible that the fluorescence becomes depolarized either before, during or after VR. A measurement of the time resolved fluorescence polarization may provide answers to these questions. The measurement of picosecond time-resolved fluorescence polarization with a streak camera was first shown by Fleming et al. 1976. With the present streak camera system use of signal averaging allows more detailed measurement of fluorescence polarization time courses and in particular a measurement of fluorescence polarization of impurity centers with long

fluorescence lifetimes. This as well as the experimental technique for these measurements is discussed in Appendix I.

2.4.2 Results for O_2

The central experimental result of fluorescence polarization measurements in this thesis is shown in Figure 2.21. The rise of fluorescence of O_2 in KBr with OG 590 cutoff filters is shown with vertical and horizontal excitation polarization in (a). In (b) the fluorescence polarization anisotropy parameter $r(t)$ is calculated according to equation I.2 in Appendix I. The result is that over the entire time period of 0 to 300 ps the polarization anisotropy has a value of 0.00 ± 0.03 . The fluorescence is completely depolarized over this time period. In order to estimate the sensitivity of this technique to polarization response time a finite response time in the horizontal component is simulated. In (c) the anisotropy time course expected with a 15 ps anisotropy decay time is shown. The anisotropy calculated assuming a 15 ps response time is much larger than the actually measured anisotropy, thus the conclusion is made that the intrinsic fluorescence anisotropy decay time of the O_2 is less than 5 ps.

The importance of this result is that it suggests that the depolarization of the fluorescence of the O_2 molecule in KBr occurs in a time which is much less than

Figure 2.21 Time resolved polarization measurement of O_2 in KBr. (a) Fluorescence rise with vertical and horizontal excitation polarizations (b) fluorescence anisotropy of (a), and (c) anisotropy which would be expected if the fluorescence depolarization time were 15 ps.

the VR time. If the depolarization occurred during the VR of the center the rise kinetics would be polarization dependent. This is certainly not observed. If the depolarization occurred after the VR the center would emit totally polarized light over the time scale of this experiment, which is also not observed.

The polarization anisotropy of the UV emission of KBr:O_2^- which was discussed in the time-resolved spectroscopy section was measured. In Figure 2.22 the result is displayed. This rise of the fluorescence at the red end (RG 665 cut) (a) is compared to the rise and subsequent decay measured with the UV filter pair (UG-11 and WG305) transmitting from 305 nm to 390 nm. In (b) the UV kinetics are shown with vertical and horizontal excitation polarization. Again the curves are identical to within the noise so the UV component is also depolarized within less than five ps.

2.4.3 Summary of Fluorescence Depolarization Experiments

Measurement of the fluorescence depolarization of the O_2^- ion in KBr has shown that the anisotropy decay time is less than 5 ps for both the red and the UV components. Anisotropy of $r(t) = 0.00 \pm 0.03$ is measured over the entire time course of 0 to 300 ps. This anisotropy decay time is short compared to the VR time of the center (about 50 ps), so a rapid randomization of the dipole takes place in less

Figure 2.22 Time-resolved fluorescence polarization of UV component of KBr:O_2 (a) rise of red component (RG645 cut) and (b) UV notch detection showing rise and decay of UV component with excitation of horizontal and vertical polarization. The similarity of these curves implies a rapid depolarization.

than 5 ps. The UV component is also depolarized within 5 ps. The theoretical interpretation of this is given in Chapter 3.

2.5 Summary of Experimental Results

The experimental results may be summarized as follows. It was found that impurities which exhibit little or no spectral structure in absorption or emission spectra exhibit very fast fluorescence risetimes (less than a few ps). Centers investigated were NaF:M, LiF:M and KBr:Tl⁺. CW spectra of absorption, fluorescence and excitation agreed well with published results indicating proper sample preparation and spectroscopic assignments. Centers which exhibit strong spectral structure showed longer fluorescence risetimes. The molecular ions O₂⁻ and S₂⁻ were studied. For the case of O₂⁻ an extensive series of measurements was carried out which showed the host, wavelength, temperature and polarization dependence of the fluorescence risetime. The reddest components of emission rise at a rate which is related directly to the VR rate of the center. Emission in the UV spectral region exhibits a fast risetime (less than 10 ps) and a decay time of about 300 ps. A strong dependence of the fluorescence risetime with the host crystal was found. This contains important information about the VR mechanism. A very weak temperature dependence of the fluorescence risetime was measured. Measurement of the time resolved fluorescence

spectrum shows conclusively the existence of hot luminescence lines which rise rapidly and decay at roughly the same rate as the ordinary luminescence rise. The number, shape, positions and intensities of these lines reveal the vibrational dynamics in the excited electronic state directly and additional spectroscopic information which is not available from conventional experiments. Fluorescence depolarization experiments reveal an extremely rapid (less than 5 ps) depolarization of the vibronic emission of the O_2^- ion in KBr and also the UV emission. The conclusion is made that the polarization of the fluorescence is lost before the primary rate-determining step in the VR process.

The use of the jitter-free streak camera discussed in Appendix I has enabled these detailed studies to be carried out. These measurements represent the first study of fluorescence kinetics of defects in alkali halides with picosecond resolution.

CHAPTER 3 THEORETICAL INTERPRETATION

3.1 Introduction

The theoretical problem of describing the VR of an impurity in an alkali halide crystal has not been solved in any detailed manner. The true solution should involve a calculation which is based on the microscopics of the system although it has not been possible to solve the problem on the microscopic level because many approximations are necessary and little is known about the electronic wavefunctions and localized vibrational modes of the defect. An alternative model is based on macroscopic or semimicroscopic equations which may be solved exactly but which cannot be related to the microscopics of the system in a direct way. A particular problem is that the semimicroscopic model (Montroll and Shuler 1957, Rubin and Shuler 1956) does not offer any estimate of the molecule-bath interaction coefficient. This parameter determines the VR rate which is of interest here. Also in this model the molecule-bath interaction coefficient is assumed to be temperature independent, therefore it can not be used to predict either the temperature or host dependence of the fluorescence kinetics.

The theoretical discussion is introduced by considering the effect of simple lifetime broadening on a vibronic transition lineshape. This discussion

illustrates the transition from strong vibronic structure to weak vibronic structure as the vibrational lifetime decreases. Several examples of fluorescence spectra in weak and strong impurity-lattice coupling limits from the literature as shown to illustrate this trend experimentally. The multilevel dynamics of the vibrational manifold are investigated with the master equation formalism of the Montroll-Shuler (MS) model. Several models of level-dependent VR rates are discussed. The scaling of the VR rate with host crystal is modeled with a coupled harmonic oscillator system. It is found that this simple model is capable of estimating VR rates of molecular ions in alkali halides quite well. In particular the VR rates predicted for O_2 are within a factor of three of the measured values. This model is extended to estimating the VR rates of S_2 and CN^- ions. An estimate of the local mode decay time results from this model. This estimate is compared to a thermodynamic calculation of heat diffusion in alkali halides, with reasonable agreement being obtained. The time-resolved fluorescence spectrum is calculated using the multilevel vibrational probabilities from the MS system. It is found that using the calculated Franck-Condon factors the intensities of the hot luminescence components differ greatly from the observed intensities. Possible explanations for this are discussed. The time-resolved

fluorescence spectrum is calculated using the number of vibrational levels as parameter.

Fluorescence depolarization experiments are analyzed qualitatively with regard to thermally-induced tunnelling transitions. The variation of the fluorescence risetime with detection cutoff energy is modeled by introducing an additional UV component the kinetics of which are derived from the UV notch filter data and the UV time-resolved spectroscopy experiments on $\text{KBr}:\text{O}_2$. This model gives a good explanation of the experimental results.

The local thermal model of VR proposed by Dexter is investigated. It is found that all the requirements for the observation of a time-dependent line-narrowing effect are satisfied by O_2 in alkali halides but the effect is not observed. The explanation for this is simple and consistent with the results of the coupled harmonic oscillator model. The excited state properties of O_2 which have been suggested by the experimental results which have been obtained here are summarized. A model for the excited states of O_2 is proposed. Finally a theory of multiphonon relaxation of a diatomic molecule in a dense medium is investigated to attempt to explain the temperature dependence of the O_2 VR rate. Some important conclusions about the VR mechanism are made.

3.2 Lineshapes

The normalized lineshape function for a transition from electronic state a to electronic state b in the adiabatic and Condon approximations is (Keil 1965):

$$I_{ab}(E) = \left\{ \sum_{\beta} |\langle a\alpha | b\beta \rangle|^2 \delta(E_{b\beta} - E_{a\alpha} - E) \right\}_{\alpha} \quad (3.1)$$

where $\{ \}_{\alpha}$ denotes a thermal average over initial vibrational states and $\sum_{\beta}$ denotes the sum over final states. This expression generates a series of delta-distributions where each delta function represents a particular vibronic transition. Such an expression can not in itself describe the details of fluorescence or absorption lineshapes since it does not include effects such as multiphonon sidebands or vibronic line-broadening mechanisms. The width of a particular vibronic transition lineshape can be written as $\Delta\nu = (\frac{1}{T_2'} + \frac{1}{T_2^*})$, where T_2' is the transverse homogeneous lifetime which results from such effects as collisions, radiative decay and spin exchange processes, and T_2^* is the transverse inhomogeneous lifetime from such processes as Doppler and strain broadening. In the case of O_2 in alkali halides the zero phonon lines of the individual vibronic transitions exhibit a Lorentzian shape with a width of about 6 cm^{-1} (Rebane and Rebane 1974). Since the lines are Lorentzian in shape, inhomogeneous processes such as strain broadening may be

neglected since they would result in a Gaussian shape and T_2^* may be neglected. If the lines were purely vibrational lifetime broadened, or their widths were determined only by the reciprocal of the vibrational lifetimes, this would imply a T_2' of 5 ps, much smaller than the 50 ps VR time which was measured for O_2 in KBr. In fact, the zero phonon lines are also homogeneously broadened as a result of the interaction with crystal phonons and pseudolocal low frequency modes. The spin-lattice relaxation time of O_2 in alkali halides is 10^{-3} s (Castner 1970) so its contribution can be neglected. It is interesting to note that although the width of the vibronic lines in the fluorescence spectrum of O_2 depend strongly upon temperature (Figure 2.4) the VR rate does not (Figure 2.14). This cannot be the result of a change in T_2' due to a change in the VR rate and T_2^* has been neglected. Thus one should write:

$1/T_2' = 1/\tau_{VR} + 1/\tau_{PH}$, where τ_{VR} is the (temperature independent) VR time and τ_{PH} is the temperature dependent vibronic line broadening lifetime induced by crystal phonons. Thus it is feasible to have a strongly temperature dependent vibronic structure with a temperature independent VR rate.

It is instructive to consider the effect of the simplest line-broadening mechanism: vibrational lifetime broadening. Such an effect arises when the lifetimes of

2X

the individual vibrational levels become comparable to or less than the crystal phonon period as a result of the rapid energy transfer to the lattice. The lineshape for lifetime broadening is a Lorentzian function of FWHM equal to the reciprocal of the lifetime. This effect can be visualized by calculating the convolution of Keil's lineshape function (3.1) with a Lorentzian function of the appropriate width. In Figure 3.1 this is shown for vibrational lifetimes of (a) 1 ps, (b) 0.5 ps, (c) 0.2 ps and (d) 0.1 ps with a 200 cm^{-1} vibrational frequency and at $T=0^\circ\text{K}$. Thus it seems plausible that centers which undergo rapid VR such as color centers exhibit little vibronic structure (a) and centers which undergo slow VR exhibit strong structure (a).

Assuming that at 0°K the initial state for the absorption process is $|g,0\rangle$ the degree of structure in the absorption or excitation spectrum should be determined by the vibrational dynamics in the excited state, in the absence of other line broadening mechanisms. Accordingly assuming that the initial state for the fluorescence transition is $|e,0\rangle$, the degree of structure in the fluorescence spectrum is influenced by the vibrational dynamics in the ground electronic state. The case of O_2 in alkali halides seems to violate these ideas. VR times of typically 50 ps were observed by measurement of the fluorescence risetimes and

Figure 3.1 Lineshape calculation with vibrational lifetime broadening and interaction of impurity with a single 200 cm^{-1} mode. Vibrational lifetime of (a) 1 ps (b) 0.5 ps (c) 0.2 ps and (d) 0.1 ps.

time-resolved spectra, but the excitation spectrum exhibits very little structure even at low temperature. Since the excitation and absorption spectra do not exhibit pronounced spectral structure even in the case of slow VR in the excited state it must be assumed that either an overlapping electronic state is involved or that some other line broadening process is active in the excited state which is not active in the ground state. One system is known (NaNO_2) which exhibits sharp structure in both the absorption spectrum and the fluorescence spectrum (Kamada et al. 1975).

In Figure 3.2 the fluorescence spectra of four impurity centers in crystalline hosts are shown: (a) V^{2+} in MgO (Sturge 1963), (b) O_2^- in KCl (Rolfe et al. 1973), (c) R' center in LiF (Fitchen 1968) and (d) F center in KBr (Fowler 1968d). The energy scales are referred to the zero phonon line. A strong zero-phonon line is observed for V^{2+} in MgO since the impurity-lattice coupling is very small (Toyozaawa 1967). The multiphonon sideband reflects primarily the one-phonon density of states and low-order multiphonon contributions. The zero-phonon line is extremely intense compared to the multiphonon sideband. For O_2^- in KCl the multiphonon sideband is considerably more intense relative to the zero-phonon line. The increased impurity-lattice coupling is responsible for this. For the R' center in

Figure 3.2 Effect of increasing impurity-lattice coupling strength. Low temperature (2 °K) fluorescence spectra of various impurities in insulating crystals. As the coupling strength increases from (a) to (d) the intensity of the zero-phonon line decreases. The degree of structure in the multiphonon sideband decreases as well due to the overlapping of high order multiphonon contributions. In the strong coupling limit (d) there is no zero phonon line and no structure.

LiF the zero-phonon line is smaller than the multiphonon sideband and the increased coupling tends to erase the vibronic structure. In the case of the F center there is no zero-phonon line and no vibronic structure due to the overlapping of high order multiphonon contributions.

3.3 Multilevel Relaxation

In order to describe the VR process by calculating the time-resolved fluorescence spectrum, risetime of the red-end emission, dynamics of the hot lines and temperature effects a model of the vibrational dynamics of the impurity/host system is required. The harmonic oscillator model of the vibrational motions of the defect and host crystal leads to a vibrational "ladder". The starting point for calculating the time dependence of the fluorescence emission is then the master equation based on the semimicroscopic approach (Montroll and Shuler 1957, Rubin and Shuler 1956) including a radiative decay term (Seshadri and Kenkre 1978) and a driving term to represent the picosecond excitation:

$$\frac{dP_n}{dt} + \alpha_n P_n = \sum_l^N (\gamma_{nl} P_l(t) - \gamma_{ln} P_n(t)) + I_n(t) \quad (3.2)$$

Here $P_n(t)$ is the probability of occupation of the n^{th} vibrational level at time t , α_n is the fluorescence decay rate from the n^{th} level, the sum runs over the N levels in the excited state, $I_n(t)$ is the time dependent

(X) excitation pulse which drives the n^{th} level and the γ_{n2} are given according to detailed balance considerations (Landau and Teller 1936) :

$$\gamma_{n2} = K(n+1) \delta_{2,n+1} + k e^{-\beta} n \delta_{2+1,n} \quad (3.3)$$

where β is the dimensionless inverse temperature $\beta = \hbar\omega/kT$, and K is the rate constant which characterizes the molecule-bath interaction. This relation allows only for transitions of $\Delta M = \pm 1$ which is the selection rule for a purely harmonic oscillator. Addition of anharmonicity results in additional selection rules but in the case of O_2 the anharmonicity is so weak (0.9 %) that these transitions can be safely neglected. Combining Equations 3.2 and 3.3:

$$\frac{dP_n}{dt} + \alpha_n P_n = K \left[(n+1) P_{n+1} + n e^{-\beta} P_{n-1} - (n + (n+1) e^{-\beta}) P_n \right] + I_n(t) \quad (3.4)$$

or in the low temperature limit which is employed here:

$$\frac{dP_n}{dt} + \alpha P_n = K \left[(n+1) P_{n+1} - n P_n \right] + I_n(t) \quad (3.5)$$

A further simplification has been incorporated into this equation which results from the long fluorescence decay times of the centers studied here. A separation of timescale for VR and radiative transitions is well justified with VR times of 10^{-13} to 10^{-10} s in systems

Figure 3.3 Vibrational probabilities in a 15 level Montroll-Shuler system excited near level 11 with a 20 ps pulse. The ground state ($n=0$) probability is delayed from the excitation pulse by an amount related to the VR rate.

with decay times of 10^{-8} to 10^{-5} s. Thus the level dependent radiative decay term α_n can be replaced with a constant small value α or the term may be deleted. It should be pointed out that the rejection of this term may not be justified in all cases. This will be discussed in Section 3.5.

The solutions $P_n(t)$ of Equation 3.5 are shown in Figure 3.3 using a Gaussian excitation pulse of 20 ps FWHM exciting near the 11th level in a 15 level manifold with a 30 ps relaxation time ($k^{-1}=30$ ps). The ground vibrational state population rises slowly after the excitation pulse arrives with a delay between the center of the excitation pulse and the 50% maximum point. In this 15 level system the delay is roughly three times the relaxation time. It is a characteristic of the MS system that the relaxation rate increases with the vibrational quantum number: the rate from the n^{th} level to the $n-1^{\text{th}}$ level is n times as great as the decay rate from level $n=1$ to level $n=0$.

One immediate result is that the shape and delay of the lowest population predicted by the 15 level system are quite different than those measured for O_2 (Figure 2.8, etc.). This feature arises from the structure of the Montroll-Shuler ladder relaxation model where population cascades from level to level. The effect of reducing the number of levels in the ladder is shown in

Figure 3.4 Ground state ($n=0$) rise as a function of the number of levels in the Montroll-Shuler system. As the number of levels increases the shape of the rise rapidly assumes a shape which is inconsistent with the measured fluorescence rise data.

Figure 3.4 with a 50 ps relaxation time. For $n=1$ the solution is the same as the three level solution discussed in Chapter 2. For a larger manifold the shape radically changes. It is impossible to fit the rise data obtained for O_2 in alkali halides using this model with more than a few levels. Therefore it seems reasonable to suggest that the VR of the O_2 molecule occurs in a reduced manifold following an initial rapid relaxation which dissipates most of the vibrational energy. An alternative explanation of this is that the level-dependent rate increases much more rapidly than the first power of the vibrational quantum number as required by the Montroll-Shuler system. For a purely anharmonic oscillator the rate increases as the square of the vibrational quantum number but the O_2 molecule is not strongly anharmonic. This will be discussed in more detail in Section 3.5.

The theory of multilevel relaxation allows a prediction of the dynamics of vibrational probabilities assuming a particular value of the relaxation rate. In addition the number of levels which are involved in the relaxation process must be known. Finally, it is not obvious that the level-dependent rates which are derived from the Landau-Teller prescription are applicable to the systems studied here.

3.4 VR Rate Scaling with Host

3.4.1 Coupled Harmonic Oscillator Model

A simple model of VR of an impurity ion in alkali halides which is capable of predicting absolute VR rates with a minimum of required information is of some value. The treatment of the vibrational motion of the O_2 ion as a harmonic oscillator has several outstanding justifications. First, the vibrational period corresponding to the intramolecular stretching mode (600 cm^{-1} in the excited state) is about 100 fs. During the VR time of 50 ps (typical for O_2 in alkali halides) the ion executes 500 to 1000 cycles of vibration, thus the motion may well be described by a harmonic model. This condition is not satisfied by the color center since VR times of less than 2 ps are indicated from this work and hence this model is probably not applicable to the case of color center VR. A second justification for the use of mechanical analogs in the case of O_2 in alkali halides stems from work by Rolfe et al. (1973) wherein a detailed calculation of the multiphonon sidebands of O_2 fluorescence spectra in several crystals was made. The model was based on the matrix of force constant changes introduced by the O_2 ion. Excellent agreement was obtained with experiment in this case with essentially a simple mechanical model. Also, since the O_2 molecule has a single vibrational mode (stretching mode) it should be

well described by a single frequency oscillator. Although the lattice has many modes of vibration (and particularly the local modes) which are important in determining the impurity-lattice coupling it is common in theories of optical lineshapes to assume that the lattice can be represented with a single frequency or an effective frequency (Longuet-Higgins et al. 1957). The effective frequency for line broadening is generally a bit less than the longitudinal optical (LO) phonon frequency. The LO phonon frequency of the host crystal is taken as the effective frequency of the host crystal in determining the coupling parameters. This turns out to be a non-critical assumption.

The equations governing the motion of the coupled oscillators are :

$$\begin{aligned} \ddot{X}_2 + \omega_2^2 X_2 + k^2 (X_1 - X_2) &= 0 \\ \ddot{X}_1 + \lambda \dot{X}_1 + \omega_1^2 X_1 + k^2 (X_1 - X_2) &= 0 \end{aligned} \quad (3.6)$$

where k is the ion-lattice coupling constant (in frequency units), ω_2 is the ion frequency in the excited state, ω_1 is the lattice frequency, λ^{-1} is the damping time of the local mode and X_2 and X_1 are the nuclear coordinates of the ion and nearest neighbor host ions, respectively. These equations are solved for the initial conditions $X_2(0)=X_0$, $X_1(0)=0$, corresponding to

the ion in the excited vibrational state and the lattice in a static configuration. Two methods of solution are used. First a perturbation solution is obtained for weak coupling ($k^2 \ll \omega_2^2$) and weak damping ($\lambda \ll \omega_2$), and second an exact solution valid for any coupling. The solution for $X_2(t)$ in the weak coupling limit is :

$$X_2(t) = X_0 \cos(\Omega_0 t) \exp(-\Omega_1 t) \quad (3.7a)$$

$$\Omega_0 = \left[\omega_2^2 + k^2 + \mathcal{O}(k^4) \right]^{\frac{1}{2}} \quad (3.7b)$$

$$\Omega_1 = \frac{k^4 \lambda}{2(\omega_2^2 - \omega_1^2)^2} \quad (3.7c)$$

Thus the impurity ion oscillates at a frequency which is slightly shifted with respect to its natural frequency ω_2 according to the coupling strength k . The ion vibration decays at a rate proportional to the fourth power of the coupling strength, the damping rate, and with a resonance denominator. This solution is not valid near resonance. The general solution is calculated by finding the roots of the determinantal equation :

$$(\omega^2 - \omega_1^2 - k^2 - i\omega\lambda)(\omega^2 - \omega_2^2 - k^2) - k^4 = 0.$$

3.4.2 Application to Molecular Ions in Alkali Halides

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Crystal	Coupling Constant k(cm-1)	LO phonon Freq. ω_{LO} (cm-1)	LO Phonon lifetime (ps)
NaCl	379	271	3.7
NaBr	327	211	3.7
KCl	376	213	3.6
KBr	334	170	8.5
KI	278	143	6.7
RbCl	363	180	3.7
RbBr	330	130	6.6
RbI	282	108	7.7
=====			

Table 3.1 Coupling constants for O_2^- ion in alkali halides as determined from frequency shifts of Raman scattering data, LO phonon frequencies of host crystals and LO phonon lifetimes of host crystals estimated from linewidths of IR absorption data.

For the estimation of VR rate scaling and absolute VR estimates a knowledge of the coupling constants and local mode decay rates is necessary. The coupling constants are readily available from the data of Holzer et al. (1968) wherein the Raman frequency of O_2^- in different alkali halide crystals was carefully measured and compared to the Raman frequency of the CN^- ion in alkali halide crystals. By extrapolating the data to a common intersection point the authors determined that the frequency of the free O_2^- ion is 1090 cm^{-1} . This procedure was required because the O_2^- ion is not stable and cannot be studied under truly isolated conditions. The coupling constants are determined from the following relation (from Equation 3.7b):

$$k = (\omega_R^2 - \omega_f^2)^{\frac{1}{2}}, \quad (3.9)$$

where ω_R is the measured Raman frequency and ω_f is the free O_2^- ion frequency. The values of the coupling constants calculated according to Equation 3.9 are shown in Table 3.1. The coupling increases with the crystal LO phonon frequency, as shown in Figure 3.5. The coupling constants are plotted with a linear regression fit which yields

$$k(\omega_{lo}) = k_0 + \eta \omega_{lo}, \quad (3.10)$$

with $k_0 = 230\text{ cm}^{-1}$ and $\eta = 0.58$.

Figure 3.5 Coupling constants for O_2^- ion in alkali halides as determined from frequency shifts of Raman scattering data and linear regression fit. This indicates increased coupling to crystals with a higher LO phonon frequency or smaller lattice constant.

3.4.3 Damping Rates

Next the damping rate of the local mode or the nearest neighbor motion is required. There is no direct measurement of this but the lifetime of crystal phonons may be estimated from low frequency dielectric function measurements of alkali halides (Martin 1965). The lifetime of crystal phonons is a reasonable first estimate of the local mode lifetime. The far infrared absorption spectrum of alkali halide crystals exhibits a sharp peak in the range of 100 to 200 cm^{-1} with a width limited by several factors. Strain broadening and the finite lifetime of the crystal phonons are the main factors. The lifetimes may thus be estimated from the absorption data by calculating the reciprocal of the FWHM of the absorption line. This will give a lower bound for the phonon lifetime. Table 3.1 also shows the lifetimes for alkali halide crystal phonons which are estimated by this method. Estimates in the range of 4 to 8 ps are obtained for the crystals studied here. These values compare favorably to the value of 8.5 ps which was measured directly by picosecond time-resolved Raman scattering in CaF_2 (Alfano and Shapiro 1971). In this case linewidth measurements indicated a lifetime of about 4 ps.

3.4.4 VR Rate Estimates

In order to estimate the VR rate of a molecular ion we consider the decay of energy of the oscillator :

$$E = \frac{1}{2} m \left[\omega_2^2 X_2^2 + \dot{X}_2^2 \right] , \text{ or} \quad (3.11)$$

$$E = \frac{1}{2} m \omega_2^2 X_0^2 \exp(-2\Omega_1 t) . \quad (3.12)$$

Thus the energy decays at a rate of $2\Omega_1$.

Application to O_2^- Ion

The calculated VR rates of the O_2^- ion in alkali halide crystals are shown in Figure 3.6. The calculated results are obtained by using the coupling constant, estimated phonon lifetime, and LO phonon frequency of each host with an excited state vibrational frequency of 600 cm^{-1} . Equation 3.8 is solved exactly in this case. The experimental points represent the reciprocal of the fluorescence risetimes of O_2^- in the long wavelength limit (Figure 2.11) in units of ps^{-1} in KCl, KBr and RbI. The overall agreement is quite good, as the estimated rates are within a factor of three of the measured values. The straight lines which are drawn illustrate the striking fact that this simple model predicts the correct scaling of the VR rate with host frequency since the slopes are nearly identical. The VR rates increase with increasing host frequency, an effect which results primarily from the increase of coupling constant with host frequency.

Figure 3.6 Scaling of the VR rate of O_2 with host. Experimental points denoted by "x" show VR rate as determined by red end risetimes measured in several crystals. Points denoted by "o" represent VR rate calculated using equations 3.10 and 3.8 with coupling coefficients and estimated local mode damping times as given in Table 3.1.

X This factor enters in the fourth power, according to Equation 3.7c, so it is the dominant factor. The following empirical relation fits the data :

$$\gamma = \gamma_0 \exp [\omega_0 / \omega_0], \quad (3.13)$$

with $\gamma_0 = 4 \times 10^{-3} \text{ ps}^{-1}$ and $\omega_0 = 83 \text{ cm}^{-1}$.

Application to S_2 Ion

For the S_2 ion the required Raman shift data is available (Ikezawa and Rolfe 1973) and the free ion frequency is 550 cm^{-1} . From these data the VR rates are calculated and shown in Figure 3.7. The slope of the VR rate with crystal LO phonon frequency is smaller than for O_2 . One experimental point was obtained for $KI:S_2$, indicated by an "x". The agreement is reasonable.

Application to CN^- Ion

The CN^- ion has a much higher vibrational frequency in the ground state: 2038 cm^{-1} (Holzer et al. 1968). The vibrational frequency in the excited state is unavailable, so the ground state vibrational frequency of the free ion is used to estimate the VR rates. In Figure 3.8 the VR rates calculated for the CN^- ion are shown. The rates are smaller than for O_2 and S_2 because the vibrational frequency is higher, and Equation 3.7c suggests that the VR rate drops as the fourth power of the frequency.

Figure 3.7 Scaling of VR rate of S_2^- ion with host. Estimated VR rates using coupling constants for S_2^- from spectroscopic data and estimated phonon lifetimes from Table 3.1. Point marked "x" denotes measured VR rate for S_2^- in KI.

Figure 3.8 Scaling of VR rate of CN⁻ ion with host. Estimated VR rates using coupling constants for CN⁻ from spectroscopic data and estimated phonon lifetimes from Table 3.1.

Figure 3.9 Scaling of VR rate of O_2^- with host. The calculated points are fit to the data using the local mode decay rate λ as a parameter which is constant for all alkali halides. Best agreement is obtained for a value of $\lambda = (2.5 \text{ ps})^{-1}$.

Local Mode Decay Rate

Calculated VR rates using the crystal phonon lifetimes which were estimated from IR absorption data are in error by roughly a factor of three. This discrepancy most likely results from the underestimation of the local mode relaxation time which enters when using the crystal phonon lifetime estimate. It is likely that the rate of dissipation of energy of the nearest neighbors is greater than that of the crystal phonons. If a constant local mode damping rate is assumed for all the crystals, the agreement is quite good for a value of $\lambda^{-1} = 2.5$ ps (Figure 3.9). It is not clear why a constant local mode decay time should provide a good fit to all the data.

3.5.4 Thermodynamic Model

A local mode damping time of 2.5 ps was determined from fitting the absolute VR rates to the experimental values. This compares to an estimate of 4-8 ps from infrared absorption data. Another way to estimate the lifetime of the local mode is to assume a continuum model for the lattice and apply a classical thermodynamic model of heat diffusion based on the heat equation :

$$\frac{\partial U}{\partial t} = \epsilon \nabla^2 U(r,t) , \quad (3.14)$$

where $U(r,t)$ is the temperature at position r and time t and ϵ is a material property given by : $\epsilon = \frac{K}{\sigma \rho}$ (3.15)

where K is the thermal conductivity, ρ is the mass density and σ is the specific heat. The solution (Carslaw 1921) assuming a delta heat pulse at $r=0$ and $t=0$ is :

$$U(r,t) = \frac{Q}{[2\sqrt{\pi\epsilon t}]^3} \exp[-r^2/4\epsilon t], \quad (3.16)$$

where $Q\sigma\rho$ is the total heat deposited in the crystal. Figure 3.10 shows the temperature distribution $U(r,t)$ calculated for NaCl at 300 °K. The heat dissipates with a characteristic decay time of a few ps. Therefore it seems that a local mode decay time of 2.5 ps which was inferred from the fitting of the experimental VR rates is physically reasonable.

3.4.6 Application to Color Centers

It seems impossible to apply this model to a prediction of the VR rate of color centers or s^2 metal ions in alkali halides. There are several reasons for this difficulty. First, a harmonic model is not justified when the VR time is comparable to the crystal phonon period and second there is no way of estimating the coupling strength of the color center to the lattice in the way which was done for molecular ions because no spectroscopic information is available about the vibrational modes.

Figure 3.10 Thermal diffusion in NaCl assuming an initial heat distribution which is a delta function in space and time. The excess thermal energy decays in a time scale of a few picoseconds.

3.4.7 Excited State Coupling Strength

The variation of the VR rate with host properties seems to be well predicted by this simple model. This contains an interesting result. The coupling strengths which were used in this model were determined from CW Raman scattering measurements. Thus the coupling strengths which are determined pertain to coupling of the ion in the ground electronic state to the lattice. The vibrational dynamics of the center which affect the fluorescence properties are those in the excited electronic state. Thus it seems that it should be invalid to use the coupling strengths determined from CW Raman scattering data in order to describe the coupling in the excited state. There is no experimental data available on the variation of the Raman frequency in the excited state with the host crystal. Only KBr:O_2 exhibits any observable spectral structure from which the excited state vibrational frequency can be determined.

In fitting the multiphonon sidebands of the O_2 ion in alkali halides Rolfe et al. (1973) found that the matrix of force constant changes in the excited state must be nearly identical to that in the ground state in order to obtain the detailed agreement which they found. They offered no explanation of why this should be but the result was clear. The result which has been obtained here, that the coupling constants in the excited state

and ground state are similar, is consistent with these findings.

3.4.8 Summary of Scaling of VR Rate with Host

Thus the measured rates of VR of O_2 in different host crystals agree quite well with the prediction of a simple physical model involving coupled harmonic oscillators. To lowest order this model predicts the correct scaling of the VR rate with host frequency requiring only the coupling constants which are easily determined from Raman scattering data. Using crystal phonon lifetimes which are estimated from far IR absorption measurements the absolute VR rates are estimated and found to be within a factor of three from the measured values. Using the local mode decay time as a fitting parameter the data can be best fit with a value of 2.5 ps. This is smaller than the estimated decay time of the crystal phonons, and agrees favorably with the prediction of a simple thermodynamic model of heat diffusion.

The success of this model despite the problem of ground state-vs-excited state coupling strengths is consistent with the results of previous researchers in fitting multiphonon sidebands of O_2 in alkali halides.

3.5 Theory of Time-Resolved Fluorescence Spectrum

3.5.1 Introduction

The time-resolved fluorescence spectrum during VR may be quite different than the CW fluorescence spectrum. Features with a lifetime of less than 100 ps which are easily detectable by the streak camera would be impossible to detect for the case of O_2 by standard photon counting techniques which have been applied to various hot luminescence studies in other systems such as NO_2 in alkali halides (Saari 1971). The time-resolved fluorescence spectrum may be calculated according to (Seshadri and Kenkre 1978):

$$I(\omega, t) = I_0 \sum_n^N \sum_m^M |\langle n|m \rangle|^2 \left(\frac{\omega_{nm}}{\omega_{00}} \right)^3 \mathcal{L}(\omega - \omega_{nm}) P_n(t), \quad (3.17)$$

where I_0 is a constant, N is the number of vibrational levels in the excited state, M is the number of vibrational levels in the ground state, $|\langle n|m \rangle|^2$ is the appropriate Franck-Condon factor connecting the m^{th} to the n^{th} level, ω_{nm} is the frequency of the transition, given by :

$$\omega_{nm} = \omega_{00} - \omega''m + \omega'n - \omega''\chi''m^2 \quad (3.18),$$

where ω_{00} is the pure electronic contribution to the transition, χ'' is the ground state anharmonicity, ω'' and ω' are the vibrational frequencies in the ground and excited states, respectively, and the excited state

anharmonicity has been neglected for lack of sufficient data in the literature. The function $\mathcal{L}(\omega)$ is the lineshape function for each vibronic transition which may contain details about the multiphonon sideband coupling and particular local modes of libration. $P_n(t)$ is the time-dependent population of the n^{th} vibrational level in the excited state as given by Equation 3.5. To complete this calculation the Franck-Condon factors appropriate to the case of O_2^- in alkali halides and the relevant spectroscopic data for the particular ion-host system are required. The purpose of this calculation will be to qualitatively model the observed features of the time-resolved spectra measured for $KBr:O_2^-$ in the visible region for which the most detailed data was obtained.

3.5.2 Franck-Condon Factors

The standard expression which is used for Franck-Condon factors of color centers (Fitchen 1968):

$$|\langle n|m \rangle|^2 = e^{-s} \left\{ \frac{m!}{n!} \right\} s^{n-m} \left[L_m^{n-m}(s) \right]^2, \quad (3.19)$$

where s is the coupling strength, $L_m^{n-m}(s)$ is the associated Laguerre polynomial, is not appropriate for the case of O_2^- in alkali halides because of the large change in vibrational frequency which results when the electronic state changes. An expression for the Franck-Condon factor for arbitrary shift and frequency change is given by (Freed, 1976) :

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$$| \langle n | m \rangle |^2 = \left(\frac{m! n!}{2^{n+m}} \right) \left(\exp \left[-\frac{25f}{1+f} \right] \right) \left(\frac{2f^{1/2}}{1+f} \right) \left(\frac{1-f}{1+f} \right)^{m+n} \\ \times \left| \sum_{l=0}^{\min(m,n)} \frac{\left(\frac{4f^{1/2}}{1-f} \right)^l}{(m-l)! (n-l)! l!} H_{m-l}(A_1) H_{n-l}(A_2) i^{m-l} \right|^2 \quad (3.20) \\ \text{, where} \\ f = \omega' / \omega'' , \quad A_1 = \left(\frac{25f^2}{1-f^2} \right)^{1/2} \quad \& \quad A_2 = \left(\frac{25f}{1-f^2} \right)^{1/2} .$$

The Franck-Condon factors calculated with this expression predict very large hot luminescence intensities. In order to qualitatively model the experimental spectra correction factors have been used. This will be discussed in Section 3.5.8.

3.5.3 Spectroscopic Parameters for KBr:O₂

The spectroscopic parameters which are known for KBr:O₂ are summarized :

$$\omega_0 = 26966 \text{ cm}^{-1} \quad \omega' = 575 \text{ cm}^{-1} \\ \omega'' = 1138 \text{ cm}^{-1} \quad \omega'' \chi'' = 8.7 \text{ cm}^{-1} .$$

3.5.4 Lineshape Function

(X) G

In order to accurately model the individual vibronic lineshapes $\mathcal{L}(\omega)$ the n^{th} order convolution of the one-phonon sideband must be calculated and summed with appropriate weighting factors depending upon the multiphonon sideband coupling strength (Rolfe et al. 1973). Since this would serve no useful purpose in qualitatively understanding the time-resolved spectra the lineshape function $\mathcal{L}(\omega)$ is taken to be a Gaussian function with a width of roughly the one-phonon sideband. A portion of the calculated CW fluorescence spectrum of

Figure 3.11 Calculated CW fluorescence spectrum of O_2 in KBr.

#

KBr:O₂ is shown in Figure 3.11. The value of s in Equation 3.20 was chosen to align the peak of this lineshape with the experimental peak.

3.5.5 Multilevel Vibrational Manifold

Since little or nothing has been previously inferred from CW spectroscopic studies of O₂ about the nature of the vibrational manifold in the excited state it must be treated as a complete unknown. Although the initial excitation at a wavelength of 266 nm is sufficient to reach the 14th level several experimental results in this work suggest that the most important vibrational levels are the few lowest. The number of levels involved in the VR process will thus be treated as a variable. Two approaches to the level-dependent rate constants are investigated. First, the level-dependent rates suggested by the MS formalism (Equation 3.5) is adopted. Then, a different approach which allows for a general distribution of level dependent rates is examined. The vibrational probabilities $P_n(t)$ for the cases considered are shown in Figure 3.12. In Figure 3.12a the excitation pulse is shown, in (b) $P_1(t)$ and $P_0(t)$ are shown for a VR rate of $k = (56 \text{ ps})^{-1}$, in (c) $P_2(t)$, $P_1(t)$ and $P_0(t)$ are shown for $k = (56 \text{ ps})^{-1}$ according to the level-dependent rates of Equation 3.5 and in (d) $P_2(t)$, $P_1(t)$ and $P_0(t)$ are shown for $k_1 = (56 \text{ ps})^{-1}$ and $k_2 = (8 \text{ ps})^{-1}$.

Figure 3.12 Vibrational probabilities for time-resolved spectrum calculation.

3.5.6 Calculation of Time-Resolved Spectrum

Case of One Level ($n=0$)

Clearly this case cannot represent the dynamics of the time-resolved spectrum since it does not allow for a finite risetime of the fluorescence.

Case of Two Levels ($n=1,0$)

In this case which provides the simplest model of the time-resolved spectrum it is assumed that excitation at 266 nm results in immediate transfer of population to level $n=1$ via a rapid process. Extra, or hot features from level $n=1$ will appear near $t=0$ at positions inbetween the ordinary features ($n=0$ lines) and decay at a rate which is equal to the rise time of the ordinary features. This is in qualitative agreement with the results of measurement (Figure 2.15) but the use of only two levels allows for only one set of extra features. In order to obtain the additional features which appear at very short times in Figure 2.15 it is necessary to add an additional level.

Case of Three Levels ($n=2,1,0$)

In this case it is assumed that excitation at 266 nm proceeds rapidly to the level $n=2$. In Figure 3.13 the calculated time-resolved spectrum with three levels for $K=(56 \text{ ps})^{-1}$ is shown using the level-dependent rates according to Equation 3.5. An additional series of lines appears at short times and decays as expected. This

Figure 3.13 Theoretical time-resolved fluorescence spectrum of KBr:O_2 with three vibrational levels ($n=2, 1$ and 0) with MS kinetics.

result is in qualitative agreement with the data of Figure 2.15 but the lifetime of the $n=2$ components using MS kinetics is greater than the lifetime of the $n=2$ features in the data. Following the MS prescription the $n=2$ component should decay at twice the rate as the $n=1$ decay. It is possible that the requirements for MS level-dependent rates are not satisfied by the O_2 molecule, so it may be reasonable to remove this restriction on the level-dependent rates in order to obtain a better description of the measured time-resolved spectrum.

A multilevel system similar to the Montroll-Shuler system is set up with arbitrary level-dependent rates k_n

(4)

$$\frac{dP_n}{dt} + \lambda P_n = k_{n+1} P_{n+1} - k_n P_n + I_n(t) \quad (3.21)$$

The time-resolved spectrum is then calculated (Figure 3.14) with all conditions the same as Figure 3.13 but using the new $P_n(t)$ obtained from Equation 3.21 with $k_1 = (56 \text{ ps})^{-1}$ and $k_2 = (8 \text{ ps})^{-1}$. In this case the $n=2$ components decay very rapidly in better agreement with the experimental spectra. Also the $n=1$ components still decay at the same rate as the $n=0$ rise. The use of an excited state vibrational frequency of $\omega' = 650 \text{ cm}^{-1}$ instead of the literature value of $\omega' = 575 \text{ cm}^{-1}$ is necessary in order to separate the $n=2$ lines from the $n=0$

Figure 3.14 Theoretical time-resolved fluorescence spectrum of KBr:O₂ with three vibrational levels ($n=2, 1$ and 0) with arbitrary level-dependent rates.

lines. The measured spectra show that the $n=2$ lines occur at a slightly higher energy than what would be predicted using the value of 575 cm^{-1} . This is not in serious disagreement with the known properties of the O_2 ion in the excited state since the present knowledge of the excited state vibrational energy is based on measurement of very small features in the excitation spectrum. In the present experiment the important vibrational energies are the separations between levels $n=2$, 1 and 0. The zero phonon line in the excitation spectrum has never been observed so the vibrational energies of these levels have never actually been determined in any CW experiments. These time-resolving measurements may be considered as the first to determine these vibrational energies.

Case of More Than Three Levels

The addition of more than three vibrational levels in the excited state creates a more complicated spectrum than that which is observed. Although it is possible that many levels participate in the VR process and are simply not detected optically because of small Franck-Condon factors, the increased manifold assuming MS kinetics affects the shape of the $n=0$ rise so it is not likely that more than three levels are important in the VR process.

3.5.7 Time-Resolved Spectrum of $\text{KCl}:\text{O}_2$

The measured time-resolved fluorescence spectrum of $\text{KCl}:\text{O}_2$ (Figure 2.20) is quite different than that of $\text{KBr}:\text{O}_2$ (Figure 2.15). The main reason for this is that the ground state is split by the crystal field by -525 cm^{-1} . Thus the spectrum consists of two sets of lines. In KCl the multiphonon coupling strength is greater than in KBr so the sidebands carry more intensity than the zero-phonon line in KCl . The time-resolved spectra of $\text{KCl}:\text{O}_2$ exhibit a risetime of about 20 ps in agreement with the previous energy-integrated results. The fact that the two sets of lines exhibit the same kinetics is further indication that they originate from the state $|e,0\rangle$ and terminate at the states $|g_1,m\rangle$ and $|g_2,m\rangle$.

3.5.8 Franck-Condon Factors for Hot Luminescence

As mentioned previously, the hot luminescence intensity components predicted with MS kinetics and Franck-Condon factors according to Equation 3.17 are in considerable disagreement with the experimental results. In this section this difficulty is discussed. A comparison of the experimental time-courses of the components I_{08} , I_{19} and $I_{2.10}$ shown in Figure 2.17 with the vibrational probabilities $P_n(t)$ shown in Figure 3.12(c and d) reveals a fair correspondence between the measured intensities and the calculated probabilities.

According to Equation 3.17 the intensities of the lines are governed by the product of the Franck-Condon factors and the $P_n(t)$. The Franck-Condon factors calculated using Equations 3.19 and 3.20 are shown in Table 3.2. The values of s (the coupling strength) are chosen so as to place the peak of the envelope at line I_{08} . A much larger value of s is required to accomplish this with the frequency-shift factor of $f=0.545$ for O_2^- , as defined in Equation 3.20. From this table we see that Equation 3.19 predicts that the hot luminescence component I_{n8} will drop rapidly in intensity compared to I_{08} as n increases. Equation 3.20 predicts that the hot luminescence components I_{n8} will increase rapidly in intensity relative to the ordinary component I_{08} as n increases. In calculating the time-resolved spectra of Figures 3.14 and 3.14 Equation 3.20 was used with correction factors of 10 and 100 to reduce the hot luminescence components I_{1m} and I_{2m} , respectively. This seemingly anomalous behavior could be tied to the rapid increase of the VR rate with vibrational quantum number that has been proposed here. Seshadri and Kenkre (1978) considered the effect of rapidly increasing Franck-Condon factors on the kinetics of the VR process. It is possible that although the fluorescence lifetime is so long for O_2^- in alkali halides the level-dependent fluorescence decay rate α_n which was discarded in

Equation	s	$ \langle 0 g\rangle ^2$	$ \langle 1 g\rangle ^2$	$ \langle 2 g\rangle ^2$
3.19	6	8.36	0.068	0.023
3.20	25 (f=0.545)	0.06	1.82	28

Table 3.2 Franck-Condon factors for hot luminescence.

Equation 3.5 may be important in determining the individual level decay rates. In this case it is not valid to calculate the MS kinetics independent of the Franck-Condon factors, as they will directly modify the level kinetics.

3.5.9 Summary of Time-Resolved Spectrum Calculations

The kinetics of the time-resolved fluorescence spectrum measured during the VR process can be reasonably well described by conventional theories. No detailed comparison of experimental and theoretical results has been attempted. One interesting result is that the rate of VR seems to increase very rapidly as the vibrational quantum number increases. An excited state vibrational frequency of 650 cm^{-1} is suggested in reasonable agreement with previous studies. Addition of more than three vibrational levels in the theory produces a more complicated spectrum than what is observed. Also, addition of more than a few levels with MS kinetics produces a shape of the $n=0$ rise which is inconsistent with measurements. The error in predicting the hot luminescence component intensities is possibly tied to the rapid increase of VR rate which may be characteristic of the excited state.

3.6 Fluorescence Depolarization

3.6.1 Introduction

The polarization of fluorescence of a defect in an insulating crystal contains information about the symmetry properties of the local environment of the center. Although generally polarized fluorescence results from the presence of the center in an optically anisotropic host it is possible to observe polarized fluorescence from an impurity center in an optically isotropic crystal. A polarization may result from a splitting of the degenerate excited state by the crystal field. This is commonly referred to as the dynamical Jahn-Teller effect (Jahn and Teller 1937).

The role of fluorescence polarization in relation to VR processes has been considered by several authors. Fukuda et al. (1967) made a detailed study of the fluorescence polarization of KBr:Tl^+ type centers and concluded that the observed polarization of fluorescence resulted from the vibronic interaction of the center with the host. They explained how polarization can be transferred from excitation to emission on the basis of multiple intersecting adiabatic potential energy surfaces in the excited state. On the basis of stress-splitting of the zero-phonon lines in the fluorescence spectrum of O_2 in KCl Ikezawa and Rolfe (1973) concluded that the O_2 molecule must reorient during the VR process because a fluorescence component perpendicular to the molecular

axis was observed even when all the molecules had been oriented in the $\langle 110 \rangle$ direction. Lütty (1968) considered the reorientation of $F_A(I)$ centers and demonstrated that the reorientation process occurs after the VR, and is primarily a property of the relaxed excited state.

It is interesting to consider for the case of O_2 in KBr (where the VR time is about 50 ps) the time dependence of the fluorescence polarization in light of these previous works. Measurement of the fluorescence polarization during the VR process provides further insight into the VR mechanism.

3.6.2 Interpretation of Experimental Result

The measurement of time-resolved fluorescence polarization of KBr: O_2 shown in Figure 2.21 indicates that the time constant for the decay of the initial polarization is less than five picoseconds. This can be regarded as the first time-resolved measurement of fluorescence polarization of a defect in alkali halide crystals with picosecond resolution. The significance of this result is that it represents a case where the fluorescence polarization is completely lost in a time which is much less than the VR time of the center. There is at present no theoretical description of the time-resolved fluorescence polarization of a defect in such an environment which can be applied to understanding this result but several qualitative explanations can be

offered. Fukuda et al. (1967) suggested that the VR process itself might cause fluorescence depolarization of KBr:Tl because the vibrational energy which is dissipated is greater than the energy barrier separating equivalent Jahn-Teller distortions. Thus the centers may very rapidly achieve a randomly oriented population. In the case of KBr:O₂ the O₂ molecule is known to undergo tunnelling transitions between equivalent $\langle 110 \rangle$ orientations at low temperature (Rebane and Rebane 1974). The barrier for these tunnelling transitions must therefore be very small. Thus the release of about 1 eV of energy during the VR process is sufficient to reorient the molecule many times over and a truly randomly oriented population may be achieved in a very short time.

3.6.3 Summary of Fluorescence Depolarization

The experimental result that the fluorescence of KBr:O₂ becomes depolarized to within a few percent with a time constant of less than five picoseconds can be qualitatively explained by considering the energy of tunnelling transitions of the molecule in the crystal. The vibrational energy which is released in the VR process is many times greater than the tunnelling barrier. For this particular case, it may be said that the fluorescence becomes depolarized well before the primary VR process, as opposed to during or after the VR process.

3.7 Scaling of Fluorescence Risetime with Cutoff Energy

3.7.1 Introduction

The scaling of the measured risetime of the O_2 fluorescence with detection cutoff energy is a result for which an incomplete explanation is offered. As in the case of the fluorescence depolarization measurements the blue-end spectral characteristics at short times measured here are poorly understood because of the lack of information about the excited states of O_2 in alkali halides. The measurements of UV end kinetics were made in two ways: time-resolved spectroscopy and UV bandpass filter technique. These measurements provide a consistent result that for O_2 a rapidly rising broadband UV emission exists with a risetime of less than 10 ps and a decay time of about 300 ps. It is centered at about 21000 cm^{-1} with a width of about 3000 cm^{-1} .

3.7.2 Interpretation of Experimental Result

The broadband UV component appears to be indirectly related to the VR process but directly related to the O_2 ion since it is not observed in pure crystals. From the preceding discussion about VR in the high vibrational levels it might seem plausible that a broadband UV emission would directly result from the cascade from $n=14$ to $n=2$. The fast risetime would be consistent with the rapid transfer of energy to the low levels which is

required by the reduced-manifold picture however this model is inconsistent with the relatively long decay time of the UV emission which was measured (Figure 2.21) since it would imply a VR time of greater than 300 ps.

It is possible that the VR process proceeds in parallel with the UV emission route rather than in series. The series model which seems more intuitively obvious requires that the rise time of the red emission is at least as great as the decay time of the UV emission whereas the parallel model does not require this. The addition of an extra fluorescent electronic state has certain justifications which will be discussed in Section 3.9. The UV component $I_{uv}(\omega, t)$ described by a Gaussian band centered at 21000 cm^{-1} with a width of 3000 cm^{-1} . The time resolved spectra are calculated with a 100 ps VR time. The energy-integrated intensity is calculated under these conditions:

$$I(\omega_c, t) = \int_{\omega_{min}}^{\omega_c} [I(\omega, t) + I_{uv}(\omega, t)] d\omega, \quad (3.22)$$

where ω_c is the cutoff frequency corresponding to the cutoff energy of the filter in use and ω_{min} is the minimum frequency of detection of the streak camera, corresponding to 850 nm. In Figure 3.15 the result of fitting the 3-level rise function to the energy-integrated intensity Equation 3.22 is shown. The fit yields a risetime of 100 ps for cut energies past the

Figure 3.15 Variation of optimized three-level fit risetime of energy integrated fluorescence rise function with UV component at 2.6 eV.

center energy of the UV component (2.6 eV), as expected. When the cut energy is increased to include the rapidly rising UV component the 3-level fit yields a decreasing risetime. The form of this is similar to the distributions shown in Figure 2.13. The details of this distribution depend on many factors such as the center, width, relative intensity and the rise and decay times of the UV component, none of which are accurately known at this point, but this nonetheless serves as a qualitative description of the behavior of the energy-integrated measurements. Thus the addition of a rapidly rising broadband UV component into the usual line spectrum of O_2 (the kinetics of which are dominated by the $n=1$ to $n=0$ decay time) indeed makes a significant difference in the energy-integrated measurements. This effect is thus not directly related to the VR process but is rather an indication of a complex excited state structure.

3.7.3 Summary of Scaling of Risetime with Cutoff Energy

The distribution of risetimes with detection cutoff energy measured for O_2 in several crystals indicates a fast rising UV component. This is consistent with UV time-resolved spectroscopy results. The disparity between the decay time of the UV component and the VR rate indicates that the components exhibit independent decay routes. The energy-integrated risetime is

calculated under these conditions. The result of this is in qualitative agreement with the experimental results which have been obtained here and this suggests some interesting properties of the excited states. These will be more fully discussed in Section 3.9.

3.8 Local Thermal Model

3.8.1 Introduction

An alternative model of VR has been proposed (Dexter 1972). This model asserts that after absorption of a photon the center instantaneously attains a high temperature. The multilevel manifold probabilities assume a Boltzmann distribution :

$$P_n(t) = \exp - [n h \omega / k_B T^*(t)] , \quad (3.23)$$

where $T^*(t)$ is the effective local temperature in the vicinity of the center. While this model provides no estimate of the behavior of $T^*(t)$ it does yield the following qualitative result. After excitation the temperature in the vicinity of the center is very high. Thus the multilevel manifold is populated up to very high levels. The emission spectrum at this time will be broad because of the large number of contributing levels. As the VR proceeds the effective temperature T^* drops, the excitation of the multilevel manifold collapses with the result that the emission spectrum narrows during the course of the of the VR process.

It is interesting to compare this model to the experimental results which have been obtained here. First, the conditions under which the model is expected to apply are reviewed. The impurity should be present in small concentration to reject the possibility of energy transfer processes. Typically densities of about 10^{17} cm^{-3} O_2 were used. There should be no photochemical reaction or internal conversion by radiationless transitions. The case of O_2 satisfies this. Excitation intensities were always well below the level at which nonlinear effects arise. Although the excited state structure may be more complicated than the two well separated electronic states which are required for the application of this theory the most significant steps in the VR process occur in a single electronic state. Use of low temperature ensures that the O_2 molecule is in exclusively the ground vibrational state of the ground electronic state. The O_2 molecule exhibits a single vibrational mode.

Two noncritical assumptions in this model are violated by the O_2 ion in alkali halides: equal vibrational frequencies in the ground and excited states and no anharmonicity. These factors do not contribute to the applicability of this model since they were only stipulated for reasons of mathematical simplicity. Thus

the O_2 ion in alkali halides should qualify as an ideal system for the investigation of this effect.

3.8.2 Application to O_2 in Alkali Halides

In order to apply this model to VR of O_2 in an alkali halide crystal further information is required. The scaling of the width of the individual lines with temperature has been measured (Figure 2.4). The broadening is related approximately linearly to the temperature above 20°K. The time-resolved spectrum is simulated under the conditions of a time-dependent broadening by assuming that the temperature $T^*(t)$ starts at a high value at $t=0$ and decreases at a rate roughly equal to the VR rate. The simulated spectrum at time t is obtained by convolving a gaussian broadening function with a width corresponding to the local temperature T^* at time t with the experimental spectrum at late times (Figure 2.15) and multiplying by the rise function $P_0(t)$ from Equation 3.5 with two levels ($n=1,0$) and $k=(100 \text{ ps})^{-1}$. For this simulation an initial temperature of 300°K was assumed (the dissipation of 1 eV into a volume of one cubic lattice constant results in a temperature of 3000°K). Figure 3.16 shows the result. At early times the spectrum is broad, and as the temperature drops the lines narrow until the temperature reaches the ambient temperature. This is then the prediction of the local

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Figure 3.16 Local thermal model prediction of time-resolved fluorescence spectrum of KBr:O₂.

thermal model of VR for O_2 assuming that the temperature $T^*(t)$ drops at the same rate as the VR rate.

This result is completely contrary to what is observed (Figure 2.15). It is found experimentally that the shape and width of the spectral lines is already well defined even before the lines have reached their maximum amplitude and the VR is complete. In other words there is no change in the width of the spectral lines as the VR process ensues. This apparent contradiction is resolved in a rather simple way. The dissipation of the local mode energy takes only a few picoseconds, a time much shorter than the VR time, as determined by fitting VR rates using the coupled-oscillator model and by the estimated thermal diffusion time in alkali halides. Over a time interval equal to the VR time the center is thus in a quasi-thermal equilibrium with the lattice. In a case where the VR time is much less than the time constant of the dissipative process it would be possible to observe the line-narrowing effect.

Therefore it is not possible to observe this line-narrowing effect for cases when the VR time is greater than the thermal diffusion time (or the lifetime of the local mode of oscillation) and to observe it in alkali halides it would require time resolution of about 0.1 ps and a VR time of less than 5 ps. It would be

difficult to do this but some possible techniques will be discussed in the Chapter 4.

3.9 Excited State Properties of O_2

3.9.1 Introduction

In this section the excited state properties of O_2 in alkali halides which can be inferred from the experimental results of this thesis are reviewed. A model is constructed which is consistent with the following measurements: excitation spectrum, CW and time-resolved fluorescence spectrum, detailed low energy fluorescence rise functions and energy-integrated risetime dependence.

3.9.2 Model

The introduction of an electronic state in addition to the $^2\Pi_u$ state which is the initial state for the vibronic fluorescence transitions is necessary to explain the UV time-resolved spectrum of $KBr:O_2$ and the energy integrated risetimes. The appearance of a broadband UV component with a fast risetime seems consistent with the notion of a very rapid VR in the high vibrational levels of the $^2\Pi_u$ state but the long decay time (300 ps) of the UV component is inconsistent with a "series" relaxation model of rate equations since it would require that the fluorescence risetime must be greater than 300 ps. In fact, risetimes as short as 15 ps are observed for O_2 in KCl. A possible parallel model is suggested (Figure 3.17) which qualitatively explains most of the properties

of O_2 in the excited state which have been observed in this thesis and elsewhere.

In this model there are two electronic excited states. The initial excitation places the ion into a state which will be referred to as the "A" state. It is quite possible that this state is composed of a dissociated molecule, such as O and O^- and the blue component represents recombination fluorescence. At present more information is required to be sure of this so a schematic approach is taken. This state is strongly coupled to the lattice leading to a rapid VR rate ("F" denotes a fast transition of less than 1 ps). The rapid VR in state "A" results in a lack of vibronic structure in the excitation and absorption spectra and a rapid rise of the UV fluorescence component from the minimum of the "A" state. At the curve crossing point between state "A" and 2u there is a probability that the ion will enter the vibronic manifold according to some branching ratio which is unimportant for the time being. The point of entry into the vibrational manifold depends on the curvatures and distortions of the excited states. This point of curve crossing may be considered as a variable. Once the center enters the vibrational manifold (the point $n=2$ is chosen) the VR proceeds as usual and the time-resolved fluorescence spectrum evolves according to the previous theories exhibiting the characteristic line structure due to vibronic transitions I_{nm} .

3.9.3 Excitation Spectrum

This model offers a good explanation for the lack of structure in the excitation spectrum. A very weak structure for $n=1$ to 5 is observed superimposed upon a broad structureless band at 2°K (Ikezawa and Rolfe 1973). No zero phonon line is observed in the excitation spectrum but clearly this model allows for the direct excitation of the lowest vibrational levels of $^2\Pi_u$ and this would explain the weak sharp structure in the low energy end of the excitation spectrum.

3.9.4 CW Fluorescence Spectrum

The details of the CW fluorescence spectrum are unchanged in this model since the initial state for the vibronic transitions on a CW basis is still the $n=0$ state of $^2\Pi_u$. The hot lines are lower than the $n=0$ lines by about 1000 times and similarly the UV fluorescence component will not be detected in a CW experiment because its lifetime is too short.

3.9.5 Time-Resolved Fluorescence Spectrum

This model provides a natural explanation for the apparent lack of hot luminescence lines for n greater than 2 in the measured TRS of KBr:O_2 . If the intersection point of state "A" and $^2\Pi_u$ is just above the $n=2$ level and just below the $n=3$ level ($28266 < E < 28916 \text{ cm}^{-1}$) then we expect the time-resolved spectrum to exhibit only $n=2, 1$ and 0 components, if the transition

to the curve crossing point is much faster than the VR rate in the high vibrational levels in the $^2\Pi_u$ state.

3.9.6 Detailed Low Energy Fluorescence Rise Measurements

The measurements of the fluorescence rise functions of O_2 in KBr in particular indicate that a multilevel theory of VR such as the MS theory discussed in Section 3.2 does not provide the correct prediction for the $n=0$ level vibrational dynamics with more than a few levels. The shape of the $n=0$ rise predicted by MS kinetics disagrees with the measurements more severely as the number of levels is increased. This result suggests that a reduced vibrational manifold in the $^2\Pi_u$ state is responsible for the shape of the rise. This could be the result of either a very rapid increase of the VR rate with the vibrational quantum number or a curve crossing mechanism with intersection near the bottom of the manifold. The VR rate can increase rapidly with vibrational quantum number in a purely anharmonic oscillator but the O_2 ion is very weakly anharmonic (0.9%) so this is not likely. Thus this model appears to support the findings of the low-energy (red end) fluorescence rise function measurements as well.

3.9.7 Energy Integrated Risetime Measurement

As discussed in Section 3.7 the introduction of a UV fluorescence component with a rapid rise (less than 10 ps) and decay time of 300 ps at an energy of 21000 cm^{-1} and width of 3000 cm^{-1} provides a qualitative explanation for the observed dependence of the risetime of the fluorescence as a function of detection cutoff energy for O_2 in KBr and KCl. For RbI the distribution is quite different but the trend is similar. The character of the UV component in terms of the location, width and intensity is dependent upon the host crystal, suggesting that it arises from the different character of the "A" state in these crystals. One might expect that the properties of this state would be very crystal-dependent.

3.9.8 Summary

Therefore the inclusion of another electronic excited state in the model of the O_2 in alkali halides seems to be justified on several grounds. It is known that the electronic states of O_2 in alkali halides can be split by the crystal field, and the case of O_2 in KCl is one where the ground state is split very strongly. It has been suggested that in KBr the excited state may be split into $2\pi_u^x$ and $2\pi_u^y$ components (Rebane and Rebane 1974), however if this splitting is the origin of the "A" state then it is difficult to understand why the two components have such different properties.

3.10 Temperature Dependence of VR Rate

3.10.1 Multiphonon Relaxation

Since the intramolecular frequency of the O_2 ion in the excited state (650 cm^{-1}) is much higher than the maximum phonon frequency of the host crystal ($100\text{--}200\text{ cm}^{-1}$) for the case of alkali halides studied the mechanism for VR may be a multiphonon emission process of order 3-6. Several theories of multiphonon relaxation have been advanced. For the case of a diatomic molecule in a dense medium Nitzan et al. (1975) have developed a theory of VR rates as a function of temperature and multiphonon order over a wide range of coupling strengths. The application of this theory to the case of VR of O_2 in alkali halides is investigated in this section. Of primary importance is an explanation of the extremely weak temperature dependence of the O_2 VR rate which was observed (Figure 2.14). The results of this investigation may contribute to a further understanding of the mechanism of VR.

3.10.2 Coupling Strength of O_2 in Alkali Halides

The multiphonon relaxation theory requires two main parameters for a determination of the temperature dependence of the VR rate: the multiphonon order N which is defined as the ratio of the vibrational frequency of the impurity molecule to the effective lattice frequency, and the coupling strength of the impurity to the lattice

$L_{\langle \nu \rangle}$. The coupling strength averaged over the crystal frequency spectrum is given by:

$$L_{\langle \nu \rangle} = \int_{\omega_{\nu}} d\omega_{\nu} \rho(\omega_{\nu}) \left(\frac{\Delta_{\nu}^2}{2} \right) \quad (3.24)$$

where $\rho(\omega_{\nu})$ is the one-phonon density of states of the host and Δ_{ν} is the normal mode expansion coefficient of the ν^{th} mode times the characteristic inverse length for repulsive forces Γ in the O_2 -crystal system. For the purpose of estimation of the coupling strength a delta-distribution for $\rho(\omega_{\nu})$ is assumed. This assumption is standard in theories of the temperature dependence of the fluorescence bandwidth of color centers. For local modes $\Delta \approx \Gamma d$ where d is the lattice constant. This coarse approximation can be improved upon but it represents an acceptable starting point. The characteristic inverse repulsive length Γ for the O_2 -host interaction is then required.

This can be obtained in a fairly straight forward manner from the coupling constant data of Section 3.4. Assuming a nearest-neighbor potential interaction of the form:

$$V(x) = \frac{V_0}{2} \left\{ e^{\Gamma(x-d)} + e^{-\Gamma(x+d)} \right\}; |x| \geq d \quad (3.25)$$

and for small displacements which are characteristic of the O_2 ion motion due to the high frequency:

$$V(x) \cong \frac{V_0}{2} e^{\Gamma d} \{ 2 + \Gamma^2 x^2 \} \quad (3.26)$$

Figure 3.18 Determination of characteristic repulsive lengths for O_2 in alkali halides.

(2) X

The nearest-neighbor interaction is quite valid in alkali-halides since the second nearest-neighbor force constants are ten times smaller in alkali halides (Cowley et al. 1963). The exponentially decaying potential is the starting point for this multiphonon relaxation theory. By writing the force distribution corresponding to this quadratic potential:

$$F(x) = V_0 e^{-\Gamma d} \{ \Gamma^2 x \} , \quad (3.27)$$

and comparing this to Equations 3.6 we can establish the connection between the coupling coefficients of the coupled harmonic oscillator theory and the multiphonon relaxation theory:

$$k^2 = V_0 \Gamma^2 e^{-\Gamma d} . \quad (3.28)$$

Plotting the k^2 values as a function of the O_2 ion-lattice distance (which is taken as the lattice constant) on a semilogarithmic scale for the eight host crystals (Figure 3.18), the slopes determine the values of Γ . The coupling coefficients squared exhibit an exponential dropoff with distance in three families: sodium, potassium and rubidium halides. This is a reflection of the interaction of the positive ions with the (negative) molecular ion. In the single frequency approximation these coupling constants are estimated by:

$$L_{\langle v \rangle} \cong (\Gamma d)^2 / 2 . \quad (3.29)$$

Crystal	Repulsive Length (Å)	Coupling Coefficient $L\langle r \rangle$
NaCl	0.54	13.6
NaBr	0.54	15.3
KCl	0.61	13.7
KBr	0.61	14.6
KI	0.61	16.7
RbCl	0.73	10.2
RbBr	0.73	11.2
RbI	0.73	12.6

Table 3.3 Repulsive lengths and estimated multiphonon coupling constants for O_2^- in alkali halides.

The values of the repulsive lengths determined by this method and the corresponding coupling coefficients are given in Table 3.3. By these estimates the values of the coupling constants are in the range of 10-15 for O_2 in the alkali halides which were studied here.

3.10.3 VR Rate General Expression

The VR rate is given by (Nitzan et al. 1975):

$$\gamma = C [1 - \exp(-\beta \hbar \omega)] \left\{ 2\pi q / [\omega \langle \omega_v \rangle (1 + q^2)^{1/2}] \right\}^{1/2} \exp(G) \quad (3.30)$$

$$\times \exp \left\{ -N \left[\ln(q + \sqrt{1 + q^2}) - (1 + q^2)^{1/2} / q - \frac{1}{2} \beta \hbar \langle \omega_v \rangle \right] \right\};$$

where

$$q = N \sinh(\beta \hbar \langle \omega_v \rangle / 2) / \hbar \langle \omega_v \rangle \quad \text{and} \quad G = \frac{\Delta_v^2}{2} \coth\left(\frac{\beta \hbar \langle \omega_v \rangle}{2}\right).$$

The lattice frequency is denoted by ω_v , the impurity frequency by ω , C is a constant, and $N = \omega / \omega_v$. This expression is valid for all temperatures in the range of the experiments and for relatively small values of N (3-6) which are used here.

3.10.4 Analysis

The application of this theory to O_2 VR will be discussed under five conditions.

Figure 3.19 Temperature dependence of multiphonon relaxation rate for coupling strengths of $L_{\langle v \rangle} = 4, 2, 1, 1/2$ and $1/4$ and medium order ($N=3$), from top to bottom.

Strong coupling ($L_{\langle v \rangle} > 4$)

In the case of a strongly coupled impurity with a medium order ($N=3$) this theory predicts a large change of VR rate with temperature (Figure 3.19). For coupling of $L_{\langle v \rangle} = 2$ a one hundred-fold increase in the VR rate is expected over the temperature range of 10-300°K, however in the experiments less than 5% variation of the VR rate was measured. This is the regime of the solution which should describe the VR rate of O_2 according to the estimates of coupling constant and multiphonon order which were made.

Low order ($\omega = \omega_{\gamma}$)

In the case where the lattice frequency is equal to the impurity frequency we have $N=1$ (Figure 3.20) and the temperature dependence is much weaker for intermediate coupling strengths. In the case of $L_{\langle v \rangle} = 4$ a much smaller temperature variation of the VR rate is predicted. This cannot be the case experimentally because the lattice has no density of states at such a high frequency (600 cm^{-1}), although it is possible that such high frequency local modes may exist.

Low Temperature ($T=10^\circ\text{K}$)

The solution (3.30) at low temperatures indicates a slow variation of the VR rate with the multiphonon order N as the coupling strength increases (Figure 3.21). The experiments with O_2 in several crystals showed that the

Figure 3.20 Temperature dependence of multiphonon relaxation rate with low order ($N=1$) due to high lattice frequency for $L_v = 4, 2, 1, 1/2$ and $1/4$.

Figure 3.21 Order dependence of multiphonon relaxation rate for low temperature and $L_{\text{vib}} = 4, 2, 1, 1/2$ and $1/4$.

(a)

(b)

Figure 3.22 Model for vibrational-librational interconversion.

VR rate changes by less than a factor of ten as the crystal frequency goes from 100 to 200 cm^{-1} , or as N goes from 6 to 3. Therefore an intermediate value of coupling strength is suggested ($L_{\langle v \rangle} = 2-4$).

Effect of Librations

With weak coupling ($L_{\langle v \rangle} = 1/2$) and medium order ($N=3$) the effect of vibrational-librational (V-L) interconversion in the O_2 molecule can be simulated. In Figure 3.22 a model for vibrational-librational coupling is shown (Mukamel 1983). A pure multiphonon coupling of the O_2 ion to the lattice is shown in (a). In (b) the O_2 vibrational motion is first converted to a large number of librations (hindered rotations) which effectively reduce the amount of energy which must be dissipated into the crystal phonons. The V-L interconversion is an inherently temperature independent process so the multiphonon order is strongly reduced by this effect. This effect can be included by defining an effective multiphonon order parameter:

$$N' = \left[\frac{\omega - p\omega_{\text{lib.}}}{\omega_r} \right] \quad (3.31)$$

where ω_{lib} is the librational frequency of the O_2 ion and p is the number of librations involved in the interconversion. In Figure 3.23 the influence of this is shown for weak coupling and medium order ($L_{\langle v \rangle} = 1/2$, $N=3$) with a librational frequency of 50 cm^{-1} as a function of

Figure 3.23 Temperature dependence of the multiphonon relaxation rate including librations. The number of 50 cm^{-1} librations is indicated next to each curve. A coupling strength of $L_{\langle \nu \rangle} = 1/2$ is used.

the number of librations p . As the number of librations increases the temperature dependence weakens as expected, but this argument does not apply for the case of strong coupling since the solution 3.30 contains a Debye-Waller factor which dominates the temperature dependence for the case of strong coupling. It should be pointed out that for the case of KBr there are no additional sharp structures at low frequency which can be attributed to librations as in other alkali halides such as sodium chloride (Rolfe et al. 1973) but it is not clear that the librations which dominate the V-L conversion process would also contribute to the fluorescence sideband spectra.

One final comment should be made. If the multilibrion order is significantly larger than the multiphonon order (i.e. if the librational frequency is much smaller than the phonon frequency) one might doubt that the librational conversion could dominate the VR process. The vibrational-librational coupling may be much stronger than the vibrational coupling to the lattice because the librations are modes of the molecule itself.

Comparison to Harmonic Oscillator Model

In Figure 3.24 the VR rate 3.30 is plotted as a function of host frequency at 10°K for several coupling strengths. The dependence is quite different than the

Figure 3.24 Lattice frequency dependence of the multiphonon relaxation rate at low temperature for $L = 4, 2, 1, 1/2$ and $1/4$.

prediction of the coupled harmonic oscillator model. There is no way that the host-dependence of the VR rate which was measured can be fit with this model for any range of coupling strength $L_{\langle \omega \rangle}$. Even in the case of weak coupling which is required to explain the lack of temperature dependence of the VR rate this model predicts a very rapid variation of the VR rate with host frequency.

3.10.5 Summary of Multiphonon Relaxation Theory Results

In summary the multiphonon relaxation theory of Nitzan et al. 1975 does not explain the features of VR which have been observed for O_2 in alkali halides. In particular the lack of temperature dependence of the VR rate is difficult to explain. The scaling of the VR rate with host is impossible to explain with this model. Several reasons can be suggested for this interesting disparity. First, the single-frequency assumption may carry much more importance than has been suggested here. The calculation of $L_{\langle \omega \rangle}$ and G should involve the actual one-phonon density of states of the crystal and actual local mode expansion coefficients. These have been tabulated by Castner (1958) for the case of a diatomic impurity in a cubic environment. A detailed calculation of the coupling constant is difficult since it requires a detailed knowledge of the dispersion relations. Also the

role of librations is poorly understood and these could significantly contribute to the disparity of the predictions of multiphonon relaxation theory and the experimental results obtained in this work.

3.10.6 Temperature Dependence of MS System

The temperature dependent factors in the MS system (Equation 3.4) which were discarded in the low temperature limit (Equation 3.5) contribute an intrinsic temperature dependence to the fluorescence kinetics. If a system can be described by a harmonic oscillator model, and thus by the MS formalism, the internal energy relaxation time t_{relax} of the oscillator is given by (Montroll and Shuler 1975):

$$t_{relax} = \left[k \left(1 - e^{-\hbar\omega/kT} \right) \right]^{-1}. \quad (3.32)$$

This is a property only of harmonic oscillators and does not depend on the initial vibrational distribution. It is simply a result of the competition between the downward relaxation and the upward effect of the thermal excitation. The temperature dependence of the relaxation time of the internal energy should then be written in generality:

$$t_{relax} = \left[k(T) \left(1 - e^{-\hbar\omega/kT} \right) \right]^{-1}, \quad (3.33)$$

where $k(T)$ is an explicitly temperature dependent molecule-bath interaction coefficient. In most

treatments no intrinsic temperature dependence is assigned to this factor. In Figure 3.25 the relative energy relaxation rate (Equation 3.32) is shown ($\kappa = 1$) for three values of the molecular energy $\omega = 200, 400,$ and 600 cm^{-1} . The relaxation rate predicted by this model decreases very weakly with temperature. This behavior is expected since the thermal excitation of the molecule competes with the VR process. On comparison of the 600 cm^{-1} calculation with the data of Figure 2.14 it is found that the prediction of this model fits the data to within the experimental error bars. Therefore the temperature dependence of the relaxation rate is contained completely within the harmonic oscillator framework, and the conclusion is made that there is no intrinsic temperature dependence of the molecule-bath interaction coefficient as defined in Equation 3.33.

3.10.7 Summary of Temperature Dependence of VR Rate

Therefore, the weak temperature dependence of the fluorescence risetime of O_2 in KBr can be accounted for with just the MS harmonic model of the impurity. Although the multilevel kinetics determined from the time-resolved spectrum measurements did not agree exactly with the MS model of level-dependent VR rates it is likely that the relation (3.32) still holds for O_2 in KBr. It is a matter of great interest to resolve the question of the temperature dependence of the

Figure 3.25 Temperature dependence of the relative energy relaxation time rate for a MS harmonic oscillator of frequency $\omega = 200, 400$ and 600 cm^{-1} . The experimental points are the relative fluorescence risetimes for O_2 in KBr.

(X)

molecule-bath interaction coefficient. On the basis of this interpretation the possibility of multiphonon relaxation must be discarded since under the conditions of O_2 in alkali halides a large temperature variation of the VR rate is predicted.

3.11 Conclusion of Theoretical Interpretation

Although no detailed theoretical description of the VR of an impurity in an alkali halide crystal is available several features of the VR process which have been revealed in this work can be theoretically justified by certain methods.

The general trend of fast VR (less than 2 ps) of impurities which exhibit little vibronic structure and slow VR (10 to 100 ps) of molecular ions which exhibit strong vibronic structure is experimentally confirmed. These results are consistent with the theoretical work on vibronic structure of Toyozawa (1967). Application of multilevel relaxation theory indicates that either the VR rate increases very rapidly with the vibrational quantum number in the excited state or that the VR takes place in a reduced manifold. A new theoretical result in this work is a simple model to describe the variation of the VR rate with the host crystal. This model predicts absolute VR rates which are within a factor of three of the measured values. This model requires coupling coefficients and local mode relaxation times which are

derived from Raman scattering and low frequency dielectric function measurements, respectively.

There is currently no model available for estimating even the relative VR rates of molecular ions in alkali halides, and certainly not the absolute rates. This model produces, to lowest order, the correct scaling of the VR rates with crystal frequency using only the Raman scattering data as input. A byproduct of this model is an estimate of the local mode decay time which is an interesting quantity for which no other information is available. The estimated local mode decay time is 2.5 ps in reasonable agreement with the prediction of a simple thermodynamic model of heat diffusion. The model was also applied to estimating the VR rates of S_2 and CN^- ions in alkali halides. For $KI:S_2$ one experimental point was obtained. The agreement with the prediction of the model is fair considering the poor signal-to-noise of the S_2 data. The success of this simple model provides justification for a harmonic model of a molecular ion in an alkali halide crystal and provides some further information about the excited state properties.

The time-resolved fluorescence spectrum can be qualitatively understood in terms of multilevel vibrational relaxation in a manifold of several levels with a certain distribution of rate constants. One puzzling difficulty with this is in the use of the

Franck-Condon factors. The components identified as $n=2$, 1 and 0 exhibit time dependence and peak amplitudes which are very similar to the vibrational populations themselves (Figure 3.12). The Franck-Condon factors required to model the time-resolved spectra should then be of the same order for hot transitions ($n=2,1$) as for the ordinary transitions ($n=0$). In fact, the Franck-Condon factors computed with either equation 3.19 or 3.20 yield incorrect results for hot luminescence lines. Arbitrary correction factors were required to bring the relative heights of the hot luminescence lines into accordance with the measured results. The origin of this difficulty is unknown.

The very rapid fluorescence depolarization of the O_2 ion in KBr (less than 5 ps) is qualitatively explained in terms of rotational energy barriers in a manner similar to that proposed to explain the depolarization of Tl^+ in alkali halides. The variation of the measured risetime of fluorescence of O_2 in energy-integrated measurements is explained with a model of the excited state which includes an additional electronic state. A model calculation indicates that the rapid change of the risetime of fluorescence with cutoff wavelengths past 2.6 eV can be attributed to the same UV fluorescence component which is detected in the UV time-resolved spectrum of KBr: O_2 .

The local thermal model of VR proposed by Dexter 1972 is investigated. It is found that although all the conditions for its applicability are satisfied by the O_2^- ion in alkali halides it is not possible to observe the time-dependent line broadening which is predicted by the model unless the VR time is significantly less than the local model thermal dissipation time. This result, when combined with the local mode decay time estimate of 2.5 ps and the measured time-resolved spectra provides a rather detailed picture of the VR process of the O_2^- ion.

A model of the excited states of the O_2^- ion is proposed which explains the excitation spectrum, CW and time-resolved fluorescence spectra and the energy-integrated fluorescence rise function measurements. This model is consistent with existing knowledge of the O_2^- ion properties. The predictions of a multiphonon relaxation theory of a diatomic molecule in a dense medium are investigated with respect to temperature dependence of the VR rate and influence of librational motions on the coupling. Some detailed disagreements are found between the predictions of this model and the experimental results obtained. These will provide the starting point for more elaborate treatments in the future.

It is found that the weak temperature dependence of the fluorescence risetime of O_2 in KBr can be explained on the basis of the MS harmonic oscillator model alone, and that an explicitly temperature dependent molecule-bath interaction coefficient is not required.

Chapter 4 Conclusion

4.1 Introduction

A significant technological advance in streak camera technology (jitter-free streak camera) has been applied to the first fluorescence dynamics study with picosecond resolution of a class of fluorescent impurities in alkali halides. This study has yielded new information about vibrational relaxation processes which govern the fluorescence properties at short times after excitation with picosecond pulses. The dependence of the fluorescence risetime with host properties, temperature, polarization and detection energy has been investigated for several impurities. In particular the first systematic investigation of the relation between the VR rate and the degree of vibronic structure of an impurity has been carried out. These results are consistent with existing notions about impurity-lattice coupling. In the case of the O_2^- ion for which the most extensive experimental results were obtained a fairly detailed description of the optical excitation process has been developed (Figure 4.1) based upon the results which have been obtained. To the authors knowledge no such detailed description of the optical excitation cycle of any impurity in an alkali halide host has been obtained previously. This figure illustrates the wide separation between the VR time (10-100 ps) and the fluorescence

Figure 4.1 Optical excitation process of O_2^- in alkali halides.

decay time (100 ns) which is typical of impurities in alkali halides. This feature makes the study of VR processes impossible with conventional techniques.

The direct time-resolving of the hot luminescence spectrum of an impurity in an alkali halide host has not been previously shown. Making use of the extensive signal averaging capability of the jitter-free streak camera detailed time-resolved fluorescence spectra of a molecular ion (O_2^-) in an alkali halide crystal during vibrational relaxation have been obtained.

For the case of strongly coupled impurity-lattice systems such as color centers and s^2 metal ions an upper limit for the VR time has been established (less than 2 ps). This represents the limit of measurement of fluorescence response time with the present system utilizing 25 ps pulses. The techniques which have been developed during the course of this thesis are directly applicable to further studies with higher time resolution, better spectral resolution and greater signal averaging capability.

Theoretically the description of an impurity molecule in a dense medium is not very complete. In theoretically understanding the experimental results which have been obtained it has been necessary to resort to a schematic rather than a systematic theoretical approach. This approach, while not providing a

satisfactorily complete description of the VR of an impurity in an alkali halide host, will hopefully form the basis for more elaborate theoretical treatments.

A new theoretical result in this thesis is the development of a simple but illuminating model of VR of a molecular ion in an alkali halide host based on a coupled harmonic oscillator system. This model predicts the correct scaling of the VR rate with host crystal-according to experiment. As a byproduct of this model the local mode decay time can be estimated. This result provides an important piece of information for the application of the Dexter local thermal model of VR. A theory of multiphonon relaxation is investigated and the conclusion is made that either the VR of the O_2^- ion is not a multiphonon relaxation (i.e. it is dominated by librational coupling) or that this impurity system cannot be described by such a simple theoretical model. The temperature dependence of the VR rate of O_2^- in KBr is contained within the framework of the MS harmonic oscillator model of VR and a temperature independent molecule bath interaction coefficient is indicated.

For the case of strong coupling of the impurity and lattice such as for color centers and transition metal ions there is no theoretical estimate of the VR time to compare to the experimental limits which have been obtained in this work. This case while still very

interesting from a theoretical point of view may be very much more difficult to model than the (already difficult) molecular ion. Two outstanding reasons for this can be given. First the O_2 ion electronic wavefunctions are well localized within the vacancy while this is not the case for color centers, and second the vibrational frequency of the impurity in the excited state is much higher than the lattice frequency, leading to a weakly coupled vibration. In the case of color centers the VR time is comparable to (or less than) the lattice phonon period. This may make the theoretical description of VR of a color center very difficult.

4.2 Applications

Applications of the results which have been obtained in this thesis will be discussed in two sections.

4.2.1 Jitter-Free Streak Camera

The jitter-free streak camera has been applied to a large variety of fluorescence dynamics studies some of which were briefly mentioned in Appendix I. In addition to applications in fluorescence spectroscopy which have been demonstrated here this technology has been used in laser fusion systems, optical ranging with millimeter precision and optical tomography applications. The increased precision and reliability of the solid-state sweep driver is of great value in these applications.

4.2.2 VR Measurements

The ability to routinely measure VR times in the range of 1 to 100 ps will have importance primarily in the development of new laser sources. In the generation of mode-locked laser pulses in the picosecond range the vibrational dynamics of the laser transitions become important. The use of molecular ion and transition metal ion stabilized color centers as laser media is very recently being discovered. It is clear that a deeper fundamental understanding of the basic physical mechanisms underlying the optical excitation cycles of these centers will have technological importance. In the case of one new laser medium (Alexandrite) significant difficulties have been encountered in producing mode-locked pulses. It is thought that the vibrational dynamics in the excited state may be responsible for the difficulty.

4.3 Suggestions for Future Study

As mentioned previously the techniques and methods which have been developed in this thesis can be directly scaled to increased time resolution, increased spectral resolution and increased signal to noise measurements leading to higher quality results. Some suggestions for system improvements will be given in this section.

4.3.1 Increased Time Resolution

The system time resolution or the width of the system response to the excitation pulse in use is dominated by the excitation pulsewidth in the present system (25 ps). This pulsewidth is limited by the modelocking bandwidth of the active-passive modelocked Nd³⁺:YAG laser. Shorter pulses (5 ps) are obtainable from passively modelocked Nd³⁺:Glass lasers but at the expense of multiple pulses and large amplitude fluctuations which would offset the advantage of the shorter pulses.

The technology now exists to amplify subpicosecond dye laser pulses to energies in the millijoule range. Preliminary results have been obtained (Yen 1983) in experiments to drive the streak camera deflection plates in the same manner as in this thesis using amplified subpicosecond laser pulses. An averaged system response width of 3-5 ps has been obtained. Thus, presuming that the stability of such a system can be maintained over a sufficiently long time period, absolute time-correlated measurements with subpicosecond accuracy should be possible with such a system. In the case of hot luminescence spectrum measurements the increased time resolution of such a system should reveal underlying structures which were not resolved in the present experiments. A new upper limit could be obtained for the

VR time of strongly coupled impurities. Several notes of caution are offered at this point. The timing errors which were discussed in Appendix II will be much more significant in these experiments and some special precautions will have to be taken in order to make measurements of fluorescence dynamics with accuracy which matches the intrinsic accuracy of the subpicosecond pulse-driven system.

4.3.2 Increased Spectral Resolution

The technique of time-resolved spectroscopy with the jitter-free streak camera system has many other applications particularly in biophysics for the study of energy transfer phenomena. Increased spectral resolution (i.e. better than the 2-3 nm which was obtained) can be obtained while maintaining a time resolution of 10 ps or better by using a double monochromator system (Frieberg and Saari 1983). The use of a double monochromator system results in a cancellation of the time dispersion effect which prevents operation at higher spectral resolution than the present single-grating system. Spectral resolution of 7 cm^{-1} has been obtained at a time resolution of 10 ps (compared to the 90 cm^{-1} in the present setup) however the throughput of such a system is not as good as the single grating system.

4.3.3 Increased Signal Averaging

The signal averaging capability of the present system is limited only by the patience of the operator. A 300 shot series requires 5 minutes to complete at the present repetition rate of one shot per second. This rate is limited at present by the OMA scanning characteristics because of the requirement of a 20 scan readout. One way to increase the signal averaging capability of the system is to increase the firing rate of the laser to the point where a different readout mode can be implemented. With a system firing rate of at least 10 Hz (which could be achieved with the present laser system with several modifications) the following readout scheme could be adopted. The cathode of the OMA could be blanked (by software) and the array filled with signal from 100 to 1000 shots. The signal could then be read out and stored. Then a shutter could be closed, the cathode blanked and the same number of background scans accumulated. The head cooler could be used in conjunction with this. The background would then be read out and subtracted from the data. The recording of the signal should be linear with intensity in this mode because the signal would not be read out between shots as in the present system.

Use of a fiber optically coupled streak camera tube should result in better statistics for single photoelectron counting and in particular a simpler amplitude histogram.

4.4 Summary

Several suggestions have been offered for future improvement of measurement accuracy. It is clear that increased accuracy will lead to a wider range of applications and a deeper understanding of the mechanisms of interaction of light and matter. The results of these studies will lead to the development of new devices and theories involving interactions at the fundamental level.

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APPENDIX I

I.1 Streak Camera

I.1.1 Introduction

The streak camera (Huston and Walters 1962) offers the possibility of detection of optical transients with time resolution of slightly less than one picosecond (10^{-12} seconds) (Bradley and Sibbett 1975). Originally developed as a diagnostic for explosions (both conventional and nuclear), the streak camera has become an important tool in the laboratory for the study of optical phenomena in the picosecond and nanosecond range. Spectral sensitivity exceeding the visible range (190 nm to 850 nm), into the infrared (out to 1.2 micrometers) and in the X-ray range (up to 30 Kev) can be obtained with S-20, S-1 and metallic photocathodes, respectively. In each case, the streak camera time resolution is roughly 100 times better than the best available oscilloscope-photodetector combination. Several other factors make the streak camera a desirable device to use. One key element is the imaging capability of the streak camera. Since it is a two-dimensional imaging device and only one dimension is required for the display of time-resolved data, one additional dimension is available for use simultaneously. This extra dimension has been used to display one-dimensionally resolved images as a

function of time, spectra as a function of time and even several beamline outputs of a multibeam fusion laser. Using this multi-track capability it is possible to simultaneously acquire up to 50 tracks of 500 point data records. This is thus a very important characteristic of the streak camera.

Electron-Optical Properties

The streak camera is a relatively simple device which is based on the photoelectric effect (Figure I.1). Light which is incident on the photocathode element (PC) causes the ejection of secondary photoelectrons out the other side (in transmission mode with a semi-transparent photocathode) which are removed and accelerated by a grid (G). These photoelectrons are then focused through the anode pinhole (A) by a focus cone assembly (FC). The anode is held at approximately +20 kV with respect to the photocathode, accelerating the electrons to a velocity of roughly one quarter the speed of light. After passing through the anode pinhole the electrons drift through a pair of deflection plates (DP) and are focused on a phosphor screen (PS). Typically a linewidth of about 100 microns is obtained at best focus, limited by imperfections in the electron-optical focusing and photocathode resolution. Application of a differential voltage to the deflection plates results in a translation of the image across the phosphor screen by an amount

Figure I.1 Streak camera tube.

proportional to the applied voltage. In a Photochron-II streak camera tube the image is translated by one millimeter for an applied bias of 40 volts. This gives a sensibility of 4 volts per resolution element. The principle of the streak camera is that the deflection voltage is ramped during the optical transient under study, and thus the time-varying intensity becomes a function of position across the phosphor screen and the resultant image is smeared or "streaked" to give a recording of its time course. The streaked image can then be recorded in a conventional time-integrating fashion such as with film or an optical multichannel detector.

The fact that the optical signal is converted to an electron image and back again by the streak camera leads to some difficulties which restrict its performance. The main difficulty is a space-charge broadening of the electron packet as it propagates through the tube. For example, a packet which propagates at one quarter the speed of light and has a picosecond time profile is confined to less than a millimeter. The packet tends to spread out in propagation as a result of the internal potential which develops when the current density exceeds a certain critical value (Friedman et al. 1976, Niu and Sibbett 1982).

Several other difficulties arise with the conversion to electrons. Scattering of electrons from the extraction mesh and deflection plates gives rise to spurious background levels and dark current from the photocathode (typically 10^{-14} amps) adds noise. Also the statistics of the detected signal may be substantially altered for the case of weak signals if the tube has low total gain (photocathode efficiency $\times$ mesh transmittance $\times$ #phosphorescence photons per 20 kV electron). It should be mentioned that a purely optical streak camera has been devised which uses an electro-optical crystal to deflect the optical beam. This device does not rely on the conversion to photoelectrons but suffers from many other difficulties. The best time resolution which has been demonstrated to date is 100 picoseconds (Ireland 1978).

Electronics Requirements

The requirement for the deflection ramp pulse can be easily estimated from the parameters which have been given. If we require a sweep speed of 0.1 mm/ps which would result in a focusing limited time resolution of about one picosecond (with 100 μ m focusing), then using the sensibility of 4 volts/resolution element the required rise is 4 volts/ps. For a linear sweep time of 500 ps (a typical requirement), we need a ramp pulse of 2000 volts rising in 500 picoseconds. The driving current required with a plate capacitance of 10 pF is $I = CV/T_r = 40$ amps.

Thus, the streak camera requires a multi-kilovolt ramp pulse of roughly one nanosecond risetime in order to obtain resolution of about one picosecond. In addition, the ramp pulse must be synchronized to the event under study to within at least the duration of the sweep in order to properly record the transient. Several methods have been devised to attempt to meet these requirements. These methods are summarized in Table I.1.

There are many methods of driving the streak camera deflection plates which satisfy the peak voltage and risetime requirements, but all have certain drawbacks. A critical issue is the synchronization of the ramp pulse with the laser pulse which excites the sample fluorescence under study. From Table I.1 it is apparent that the first four methods result in significant jitter. Significant jitter can be defined as jitter which is greater than the excitation pulse width in use. For thirty picosecond pulses (a common pulsewidth of a modelocked $\text{Nd}^{3+}:\text{YAG}$ laser) methods 1-4 lead to problems. Methods 3 and 4 are the only ones in use today in commercial streak cameras. The jitter in these devices originates in the statistics of the avalanche process itself. An avalanche device once triggered generates a voltage waveform the shape, timing and amplitude of which are determined by the particular characteristics of the device such as age, temperature, etc. Variability in these characteristics as well as the

Method	Voltage (kV)	Risetime (ns)	Jitter (ps)	Drift
=====				
Krytron	4.0	3-5	500-1000	yes
Spark gap	15	2-5	200-1000	yes
Avalanche stack	3.0	2-5	30-100	yes
Ceramic triode	3.0	3-100	(50-100)*	yes
Photoconductive	6.0	0.5-1.5	2	no
RF	3.0	(10 ns sine)	10	yes
=====				

* driven by avalanche transistors

Table I.1 High voltage nanosecond risetime electrical pulse generators for streak camera applications.

actual avalanche process leads to jitter from shot to shot. The overall reliability of these devices is not acceptable for routine use. The internal delay in these devices may change slowly over an extended time period such as a day or during a power-down cycle. This slow drift of the time origin introduces uncertainty into the experimental process and makes detailed comparisons between data sets taken at different times difficult. This problem is of particular importance in laser fusion systems where one shot is taken every one half hour and an entire data set may be missed.

The problem of jitter and drift has been virtually eliminated by the use of a photoconductive bulk semiconductor switch developed in this thesis. With modest trigger energy requirements ($100 \mu\text{J}$) the device greatly improves the performance of the streak camera and has enabled many detailed studies to be carried out by extensive signal averaging.

The last type of sweep driver considered here is an RF device which uses a synchronously pumped modelocked dye laser to generate a periodic deflection of the electron beam in synchronism with the arrival of the modelocked laser pulses (Sibbett 1982). This scheme is completely complementary to the jitter-free deflection system which operates at low repetition rate (1-500 Hz) because it operates at high repetition rate (100-200 MHz). The

individual pulses from the dye laser are very weak (10^{-11} J) and excite extremely weak individual fluorescence signals. The high repetition rate compensates for this weakness by averaging many shots (10^8 shots). This system is not applicable to the study of fluorescence with decay times (10^{-7} to 10^{-5} seconds) which are characteristic of the systems studied in this work.

Summary

In summary, the electronics requirements for sweep generation are not well met by conventional methods for the fastest sweep speeds which are required for picosecond resolution. The jitter-free deflection circuit developed in this thesis has provided an important contribution to streak camera technology and in particular has enabled a detailed study of the fluorescence dynamics of very weak signals with fast risetimes (risetimes of less than 25 ps) for the first time.

I.1.2 Sensitivity

Spectral

Streak camera photocathodes for operation in the visible range are generally multi-alkali semi-transparent substrate of the S-20 type. Figure I.2 shows the spectral sensitivity of a typical streak camera photocathode. Special S-5 response photocathodes are available which extend response out to 940 nm. Ultraviolet response extends down to the entrance window cutoff (in the case of

Figure I.2 Optical responsivity of standard S-20 streak camera.

(59) X
our streak camera fused silica) which allows response down to 200 nm. Quantum efficiency approaching 5% can be obtained. The response in the near infrared is limited to 1.2 μm for an S-1 response cathode. It should be mentioned that this represents a significant limitation to the general study of color center fluorescence with picosecond time resolution using streak cameras since F-centers emit in the spectral range 0.8 μm to 1.4 μm and F_A centers emit in the range 1.0 μm to 2.5 μm . If photocathodes could be made in the near infrared range, they would have to be cooled to reduce dark current to an acceptable value. This would be technologically very difficult to implement.

Polarization

The streak camera photocathode is not a polarization sensitive detector. This is an important point because all other methods which have been devised for the measurement of fluorescence with resolution of a few picoseconds require the detection of only one polarized component. This makes polarization measurements easier and allows the detection of unpolarized time courses if necessary. The response of the streak camera/lens system exhibits less than 5% of intrinsic anisotropy in response to vertical and horizontal polarizations of light. Techniques for time-resolved polarization measurements will be discussed in Section I.1.3.

Incidence Angle

The photocathode does not have a strongly varying response with the angle of incidence of light, so it will accept a large solid angle of fluorescence. This means that fast optics (low $f/\#$) can be used to optimize collection sensitivity. Again, this is important to note in relation to other methods of picosecond resolution fluorescence detection methods since they accept only a small solid angle and thus suffer from reduced light collection efficiency and complex experiment dependent alignment requirements.

Summary

The relative response characteristics of the techniques of Kerr gating (Duguay and Hansen 1969) optical mixing (Hallidy and Topp 1977) and streak camera detection of general fluorescence transients are compared in Table I.2. Since the first two can be considered purely optical techniques, they are inherently jitter-free. That is to say that the synchronization of the gating window with the signal which is to be sampled does not change in a random and unpredictable way. This is an important consideration for detailed picosecond kinetics work. The streak camera, on the other hand, is the most general detector of fluorescence and has multi-track or imaging capabilities as well. The jitter problem is the most serious problem with the conventional streak camera. In the case of the

Method	Spectral Bandwidth	Polarization Response	Solid Angle Acceptance
=====			
Nonlinear Mixing	Restricted	Highly Restricted	Highly Restricted
Kerr Shutter	Not Restricted	Highly Restricted	Restricted
Streak Camera	Not Restricted	Not Restricted	Not Restricted
=====			

Table I.2 Relative response characteristics of three methods of fluorescence measurement with time resolution of a few picoseconds.

jitter-free streak camera, one has a truly versatile and accurate means of recording and quantitatively characterizing picosecond fluorescence events with a timing accuracy of one picosecond.

I.1.3 Measurement Techniques

Time Resolved Fluorescence

A typical measurement with a streak camera consists of exciting a sample S (Figure I.3) with a picosecond laser pulse and collecting the fluorescence with a lens L, forming an image on the photocathode PC. The fluorescence can be filtered through interference filters IF for narrow-band kinetics measurements. For many purposes, fluorescence at all wavelengths past a set cutoff wavelength is detected using a glass filter F. These filters block greater than 10^5 for wavelengths below their cutoff value, transmit greater than 90% above the cutoff and have a transition region of only 20 nm from 10% to 90% transmission. The most critical function of the blocking filter is to suppress scattered excitation light, which may be 10^4 times greater intensity than the fluorescence light. Neutral density filters ND may be required in the case of strongly fluorescing samples or for the attenuation of scattered excitation light for time origin determination. In this imaging geometry the spot size of the fluorescence may be large enough to restrict the time resolution of the measurement. This is a result of

Figure I.3 Optical configuration for picosecond time-resolved fluorescence measurements at cryogenic temperatures.

directly imaging the fluorescence onto the photocathode instead of using an intermediate slit as is conventionally done. In the case of the jitter-free streak camera much faster sweep speeds are obtainable than those of the commercial streak cameras so the focusing requirement is not as severe. The use of this geometry results in simpler alignment, higher throughput and fewer intermediate optics to act as losses and scattering sources.

Time-Resolved Polarization

The time-resolved polarization of fluorescence signals contains a great deal of information about molecular diffusion (Fleming et al. 1976). In the case of molecules in solution, the reorientation of molecules as a function of time can be directly measured with a streak camera. In Figure I.4 the optical setup required for a picosecond time-resolved fluorescence polarization measurement is shown. There are two complimentary methods for measuring the polarization. The first involves the use of excitation with fixed polarization and an analyzer polarizer P of variable orientation. With vertically polarized excitation, the required number of shots is accumulated with the analyzer set in a vertical position. This is stored and the same number of shots is accumulated with the analyzer in a horizontal position. The

Figure I.4 Optical configuration for time-resolved fluorescence polarization measurements at cryogenic temperatures.

fluorescence polarization anisotropy ratio is then calculated using :

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2 I_{\perp}(t)} \quad , \quad (I.1)$$

In this equation, the factor of 2 in the denominator comes from the fluorescence polarized in two directions orthogonal to the excitation polarization, only one of which is detected. Using this technique, anisotropy curves have been measured to an accuracy of a few percent. A technique for measuring the two time-dependent polarizations simultaneously on each laser shot was developed to compensate for laser energy fluctuations (Podolski 1982).

The other technique requires no analyzer polarizer and results in higher signal-to-noise ratios. The total fluorescence signal is detected with first vertical excitation polarization and then horizontal excitation polarization. The anisotropy is then given by :

$$r(t) = \frac{I_v^T(t) - I_h^T(t)}{I_v^T(t) + I_h^T(t)} \quad (I.2)$$

The excitation with alternately vertical and horizontal excitation polarizations is easily accomplished with a Babinet-Soleil compensator set to exactly one half wave retardance at the excitation wavelength. For UV

fluorescence polarization measurement, the signal may be up to three times as big as the signal obtained with the analyzer polarizer technique because even the best UV Polaroid filters only transmit about 35% in the direction parallel to the polarizer axis. One useful feature of the anisotropy parameter $r(t)$ is that it automatically compensates for nonuniform response across the streak camera field since it is defined as a ratio of the two signals which are equally affected by the nonuniform response. If there is a nonlinear intensity response in the system to incident intensity (Section I.5) then the two polarization signals $I_{||}(t)$ and $I_{\perp}(t)$ must be individually corrected before forming the anisotropy ratio. This effect is not cancelled by the anisotropy ratio and has the effect of reducing the measured value of anisotropy while not changing the kinetic result drastically.

In the use of the technique of unpolarized detection with alternate excitation polarizations, the intrinsic polarization sensitivity of the streak camera/lens system must be determined and taken into account for accurate absolute readings. This can be measured by inserting the analyzer polarizer and comparing the intensity with excitation vertical and polarizer vertical with excitation horizontal and polarizer horizontal. The difference in these signals reflects the intrinsic sensitivity of the

streak camera/lens system to polarization. In practice, less than 5% difference is observed.

Time-Resolved Spectroscopy

As mentioned earlier, the streak camera can be used to display data along the direction orthogonal to the streak direction. In order to measure the fluorescence spectrum at various time intervals a spectrometer is used to disperse the fluorescence signal along the "slit" direction of the streak camera photocathode (Figure I.5). In this case, a grating spectrometer is used to obtain good spectral resolution, although a prism spectrometer could also be used for low resolution spectroscopy. Fluorescence from the sample S is collected by a lens L, while the transmitted excitation beam is blocked by a beam block. The spectrometer images the slit SL onto the photocathode PC. Diffraction grating G provides the spectral dispersion. Care must be taken that the time resolution is not spoiled by the time-dispersive nature of the diffraction grating in this experiment (Robinson et al. 1979, Schiller and Alfano 1980). This effect places a limit on the spectral resolution obtainable while simultaneously achieving picosecond time resolution. In practice, spectral resolution of about 2-3 nm can be obtained at 25 picosecond resolution with the single grating spectrometer.

Figure I.5 Optical configuration for time-resolved spectrum measurements with single grating spectrometer.

The streak camera in this case generates continuous distributions in the spectral direction and time direction, so a two-dimensionally resolving detection system must be used to acquire all the data. A fully two-dimensional detection is not necessary in the case of time-resolved spectroscopy with the jitter-free streak camera. Since the jitter-free streak camera can be set to an absolute time origin for averaging many shots, one slice of temporal information can be measured and stored to later reconstruct the time-varying spectrum. The OMA in this case is rotated by 90 degrees with respect to its normal direction with the scan direction parallel to the time axis. This places the scan along the direction of wavelength dispersion. The spectrum is thus directly measured with a gate time corresponding to the scan height (ΔY) divided by the sweep speed. The time origin is determined by the scan position (Y_0) and the setting of the delay line. Either can be varied to map out the time-variation of the spectrum. The method of delay line variation results in more accurate spectroscopic data because of two factors. First, the same scan region on the OMA is used for all spectra so that scatter and longtime retracing corrections can be taken once and used to correct all spectra. Second, in the case of time origin variation by movement of scan origin Y_0 , the field curvature and "S" distortion in the intensifier and OMA

contribute to errors in the wavelength calibration which are impossible to compensate for. In the case of time origin change by variation of delay line setting the wavelength axis remains rigorously fixed as the delay time is changed.

I.2 Picosecond High Power Switching

I.2.1 Device Principle

The generation of picosecond electrical impulses with picosecond laser pulses using bulk photoconductivity in semiconductors was first shown by Auston 1975. The idea is very simple: optically implanting charge carriers into the bulk of a high-resistivity semiconductor results in a photoconductive current signal. One of the most important features of this signal is that it is precisely synchronized with the laser pulse which is used to excite the device. As mentioned before, no conventional electronic device is capable of producing an electrical pulse of perfect synchronization to a trigger pulse. This remarkably simple technique will be described with regard to sensitivity, risetime and power handling capability.

Optical Sensitivity

The picosecond high power photoconductive switch (Figure I.6) requires typically a few hundred microjoules of incident optical energy at 1064 nm (Mourou and Knox 1979) in order to achieve an on-state resistance of a few ohms which is necessary for efficient switching. The

Figure I.6 Picosecond high-power photoconductive switch in 50 ohm coaxial configuration.

required optical energy increases as the gap length increases while the high voltage holdoff capacity also increases as the gap length increases. This tradeoff of switching sensitivity with holdoff capability is of critical importance. An energy of a few hundred microjoules in a 25 ps pulse is easily available in any modelocked Nd³⁺:YAG laser system.

Switching Risetime

Since the switching mechanism is purely photoconductive there is no intrinsic limitation to the risetime of the switched signal. Electrical pulses with risetimes as short as 690 fs have been generated and measured using GaAs:Cr excited by 100 fs dye laser pulses (Valdmanis et al. 1983). In the case of the streak camera deflection application a fast rising electrical signal is not desired so this consideration is not important. The risetime of the electrical ramp signal in the deflection circuit will be discussed in Section I.5.

Bias Requirements

In the case of intrinsic silicon, the relatively low bulk resistivity (10^4 ohm-cm) leads to bulk heating and thermal avalanche when the device is biased at more than a few hundred volts DC. This problem can be overcome by biasing the gap with a pulse of microsecond duration (Mourou and Knox 1979). The bias is then only applied for an interval in which the temperature rise in the device is

too small to permit thermal avalanche. By synchronizing the bias pulse with the laser pulse the bias can be applied just prior to the arrival of the picosecond laser pulse which activates the device. This technique works well but requires a separate high-voltage (1-10kV) stable pulse generator. The synchronization may represent a problem if operating with a non-actively Q-switched laser, because a stable pre-trigger pulse may not be available. Semiconductors such as GaAs:Cr, CdS, InP:Fe and $\text{CdS}_x\text{Se}_{1-x}$ have high enough resistivity to allow DC bias at up to 6 kilovolts even at room temperature if a large enough gap is used. An accurate method to determine the threshold of thermal instability is to measure the current-voltage characteristic of the gap with a DC bias. In Figure I.7 the current-voltage characteristics for 1/2mm and 2mm gaps of CdS are shown. The point of departure from a linear dependence of current with voltage indicates the threshold of bulk heating. This places an upper limit on the DC room-temperature operating capability. A reasonable rule of thumb for bias capability of direct-gap high resistivity semiconductors is a holdoff of one kilovolt per millimeter of gap.

Power Handling Capability

For the case of a multikilovolt bias and a 50 ohm load impedance the switched power is of the order of 10^6 watts. Electrical powers of megawatts can be switched

Figure I.7 Current-voltage characteristics of CdS gaps at 300°K.

with only several hundred microjoules of laser energy. This creates a current density of about 2000 Amps/cm² in a typical device. Despite these seemingly large figures, these devices have been found to have a long lifetime. This is in part because the current is effectively uniform throughout the bulk of the device when it is excited at an optical energy below the band gap of the semiconductor. This leads to bulk absorption ($\alpha = 10 \text{ cm}^{-1}$ for intrinsic silicon at 1064 nm excitation wavelength). In the case of excitation above the bandgap the absorption depth may be less than 5 microns, leading to a current density of 10⁵ Amps/cm². The linear photoconductive process works without the formation of high current density filaments such as those in avalanche switching devices. These high current density filaments create damage in the crystal which leads to a degradation of the device performance. The picosecond photoconductive switch has as large a power handling capability as that of conventional switching devices, but a much greater operational lifetime.

Timing Fluctuations

If there is any variation in the width or shape of the excitation pulse we expect a small amount of jitter between the electrical pulse and the excitation pulse. For energy approaching the saturation energy, the time origin shifts earlier by as much as one full-width at half maximum (Mourou and Knox 1980). If the energy fluctuates

a jitter will result. The magnitude of this effect is less than 0.1 FWHM for all energies less than 100 times the 50% efficiency level. In the case of a 30 picosecond FWHM laser pulse, this corresponds to a maximum shift of 3 picoseconds in the case of full saturation. This is thus not a very significant effect. A further timing fluctuation results from pulsewidth fluctuations. If the FWHM fluctuates by 10% the delay will fluctuate by 10% so this effect is of the same order of magnitude, or 0.1 FWHM. Taking both effects into account, we expect a jitter of a few picoseconds with reasonable laser energy, shape and pulsewidth fluctuations.

Voltage Fluctuations

The fluctuation in voltage will be smaller than the fluctuation in laser energy as the energy approaches the saturation energy of the gap. In applications such as the jitter-free streak camera shot-to-shot voltage stability must be better than 1% to obtain jitter-free operation. The energy level which is required to operate the device far enough into saturation to achieve a particular level of fluctuation can be estimated (Knox et al. 1983). Typically for a 20% fluctuation we require an energy of 20 times that required for 50% switching efficiency to maintain 1% voltage fluctuation. In this way it is possible to generate stable voltage pulses using unstable laser energies even though the photoconductive mechanism

is a linear process. Applications of picosecond high power switches have been reviewed by Mourou et al. (1982).

I.3 Jitter-Free Streak Camera

I.3.1 Improvement Over Existing Technology

The reduction of trigger jitter solves the major operational difficulty with the streak camera. In this section the importance of jitter in detection of picosecond optical events with a streak camera is discussed.

Importance of jitter reduction

The effect of jitter in a signal averaging system is to increase the width of the time response function of the system. Equation I.3 expresses the relation between the width of the impulse response function after averaging many events τ_A , the focusing-limited time resolution τ_o , defined as the focusing resolution divided by the sweep speed, the jitter distribution width τ_j , and the optical pulsewidth τ_p :

$$\tau_A^2 = \tau_o^2 + \tau_p^2 + \tau_j^2 . \quad (I.3)$$

For the case of $\tau_j > \tau_p$, significant distortion of the pulse profile is obtained. In Figure I.8 the effect of jitter on the measurement of the averaged excitation pulse is shown. This is a numerical simulation for the case of $\tau_p = 20$ psec, $\tau_o = 5$ psec, for gaussian pulses and (a)

Figure I.8 Effect of jitter in direct accumulation averaging operations (numerical simulation).

single pulse, (b) a 20 pulse summation with $\tau_j = \pm 100$ ps, and (c) a 20 pulse summation with $\tau_j = 2$ ps. The effect of the jitter is to give an unreliable measurement of the true pulshape (a). In the case of $\tau_j = 2$ ps the width is only increased from $\tau_A = 20.62$ ps to $\tau_A = 20.71$ ps by the 2 picosecond jitter.

This analysis was based on the assumption that the jitter is not compensated between shots before summation. One technique has been developed to deal with the jitter problem by adding a marker pulse early in the streak (Campillo et al. 1977). After each shot, the marker pulse is located manually and shifted to a reference location.

Definition of Jitter-Free Deflection

The condition for jitter-free deflection may be defined through Equation I.3. The basic requirement is that the jitter have an insignificant effect on the width of the system impulse response function, or:

$$\tau_j^2 \ll \tau_o^2 + \tau_p^2 \quad (I.4)$$

In the case of $\tau_o = 5$ ps and $\tau_p = 20$ ps this condition is certainly satisfied, but in the case of $\tau_o = 1$ ps, $\tau_p = 1$ ps and $\tau_j = 2$ ps the condition is not satisfied.

I.3.2 Three Methods of Switching Applied to Streak Camera

Intrinsic Silicon

The first demonstration of jitter-free deflection of a streak camera (Knox et al. 1979, Mourou and Knox 1980) utilized intrinsic silicon as the picosecond high power switch material. In this experiment (Figure I.9) the deflection ramp pulse was generated by a silicon switch integrated into a coaxial line. The charge-line geometry was adopted and the switch produced a 20 nanosecond long square pulse which propagated down a coaxial 50 ohm line. The line was connected to the deflection plate of the streak camera and terminated with a 50 ohm load. The charge-line was charged with a 20 microsecond pulse from a microwave triode pulse generator. This pulse length was chosen because it is less than the thermal instability buildup time (about 50 μ s) and longer than the Q-switching jitter in the laser trigger (about 5 μ s). Jitter of 2 ps was obtained with this technique but the synchronization of the bias pulse with the laser train had to be constantly monitored to be sure of proper operation. This proved to be inconvenient, and a further problem arose because of this. If the high voltage bias pulse is not perfectly flat the bias voltage on the charge line at the moment of discharge will vary according to the slope of the pulse and the jitter of the Q-switched envelope. The

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Figure I.9 Jitter-free streak camera driven by pulse-biased silicon switch in 50 ohm coaxial configuration.

use of a switch which can be DC biased and operated at room temperature would be preferred for this reason. In addition the use of a DC supply would result in a simpler system to implement and operate with freedom from synchronization requirements.

A krytron-biased silicon switch was used to deflect a streak camera (Margulis et al. 1980). Jitter of 15 ps was obtained. Fluctuations in the voltage, shape and timing of the krytron pulse contributed to this figure.

Gold-Doped Silicon

A method to bias a silicon switch with DC in the multikilovolt range was found (Stavola et al. 1980) and applied to the streak camera deflection problem (Stavola et al. 1980). This technique involved the use of silicon which was doped with gold (a deep impurity in silicon) cooled to liquid nitrogen temperature. It was found that intrinsic silicon when cooled to 77°K exhibited a large increase in resistivity and a low dielectric breakdown field strength (100V/cm). This was attributed to the large mean-free path of the carriers in the highly pure material in the absence of electron-phonon scattering at low temperature. The addition of gold increases the dielectric breakdown strength so that up to 4 kV could be held off at 77°K. A stripline geometry was adopted to facilitate heat sinking the switch. The electrical pulse was used in the same way as the intrinsic

silicon-generated pulse to drive the deflection plates of the streak camera tube. It proved possible to obtain 2 ps jitter with this method as in the case of the intrinsic silicon but the device in this case could be DC biased. The operational difficulty of maintaining the device at 77°K proved detrimental to the routine use of this technique and a simpler method which could operate with DC bias and at room temperature would be still preferable.

Chromium Doped Gallium Arsenide

Gallium arsenide doped with chromium (a deep impurity) exhibits very high resistivity (10^8 ohm-cm), high mobility ($2000 \text{ cm}^2/\text{V-s}$) and high dielectric breakdown field strength (10^5 V/cm) (Lee 1977). It can be biased at up to 1 kV per millimeter of gap length and efficiently switched with excitation at 1064 nm (Mourou and Knox 1979), the fundamental wavelength of $\text{Nd}^{3+}:\text{YAG}$. The GaAs:Cr could not be used in the same 50 ohm geometry as the previous two methods for driving the streak camera because it has a short carrier decay time (1 ns). This would result in a rapid retracing of the electron beam (a few nanoseconds after the initial sweep) and any fluorescing signals with a decay time of more than about 1 ns would cause a retracing background, leading to inaccurate recording. The removal of the condition of 50 ohm termination and impedance matched geometry solved this problem. Using a high impedance termination on the plates

(✓)

the retracing time is extended to 100 microseconds (Knox and Mourou 1981). The experimental configuration for implementation of this is shown in Figure I.10. With a termination resistance of 5 megohms the deflection plates discharge with a 50 μ s time constant. The sweep rise occurs in roughly one nanosecond and can be quite linear.

The result is a simple to operate, reliable sweep deflection device. With DC bias there is no synchronization problem and operation at room temperature simplifies the routine use of the device. The switch material is commercially available (MACOM Associates, Inc.) and inexpensive (\$2.00 per device). The switch contacts do not have to be elaborate, ordinary silver paste contacts are the best. One device has been in continuous operation since 8/80 with no indication of failure. This is expected for a linear photoconductive device.

Summary

A summary of the main parameters relating to picosecond high-power switching applied to streak camera deflection is given in Table I.3. While the DC biased GaAs:Cr is the easiest of these to implement and operate, it is difficult to obtain sweep risetimes of longer than about 1.5 nanoseconds without introducing ringing. In the case of the other two methods conventional in-line integrators can be used to directly obtain longer linear

Figure I.10 Jitter-free streak camera driven by DC biased GaAs:Cr switch at room temperature.

sweeps. The jitter-free deflection is however primarily important at the high sweep speeds which require sweep risetimes of 0.5 to 1.0 nanoseconds.

I.3.3 Applications

A brief review is given of the applications in which the jitter-free streak camera has been used to detect picosecond fluorescence. In every application the signal averaging capability afforded by the jitter-free deflection has proved to be of significant value in obtaining higher signal-to-noise ratio than in single-shot measurements.

Solid State Physics

In solid state physics applications, the jitter-free streak camera was used to make the first measurement of fluorescence of an amorphous semiconductor (Weinstein et al. 1983). The temperature dependence of the fluorescence decay rate of a-As₂S₃ was measured in a series of 300 shot averages. In this case the single-shot data consisted of individual photoelectron events from the photocathode. This represents a case of signal averaging in the limit of vanishing signal. This situation will be discussed in more detail in Section I.7. The fluorescence of cis- and trans-polyacetylene was measured (Andrews et al. 1983) for the first time. In this case an extremely rapid initial decay (less than 5 ps) was found. The absolute timing capability of the

Material	Max. Bias (kV)	Bias Type	Device Temp. (K)	Recomb. Time	Config.	Retrace Time
Silicon	10.0	Pulsed	300	10 μ s	Charge line	20 ns
Au:Silicon	4.0	DC	77	50 ns	Strip line	5 ns
Cr:GaAs	6.0	DC	300	1.5 ns	High Imped.	100 μ s

Table I.3 Picosecond high power semiconductor techniques applied to the streak camera deflection problem.

streak camera in jitter-free averaging mode was critical in this experiment.

Biological Physics

In the area of biological physics, many studies have been performed which have directly benefited from the signal averaging capability of this system. The process of exciton annihilation in Chlorophyll A/B proteins was studied over a wide range of intensities (Nordlund and Knox 1981). Fluorescence depolarization of ethidium bromide/DNA complexes (Magde et al. 1983) and decay kinetics of Hematoporphyrin derivative were studied (Hanzlik et al. 1983).

Chemistry

Studies in chemistry have been performed on kinetics of phthalazine fluorescence (Anderson and Knox 1981), and fluorescence depolarization of rhodamine dyes (Podolski 1982).

I.4 Optical Multichannel Detection

I.4.1 Methods Available

The extraction of quantitative information from a streak camera requires some kind of optical readout system which records and digitizes the intensity distribution produced by the streak camera tube. Several methods can be used: film, reticon array or vidicon tube system. These methods will be briefly discussed.

Film

For the purpose of fluorescence measurement, film is not a practical method of recording, primarily because of the inconvenience of processing and densitometry. Also, multiple-shot linear averaging can not be done with film. From a point of view of information capacity film greatly exceeds the capacity of all present electronic recording media with the ability to record as many as 10^8 pixels in a $1/2$ " square segment. Dynamic range is extremely good (about 10^4 for Triax film). In these respects film far exceeds the capabilities of the streak camera itself so it is not necessary to require the use of film in this application. In some applications requiring two-dimensional recording with infrequent shot cycles such as for X-ray streak camera recording of laser induced implosions film is by far the best choice for recording. The nonlinearity of density response with respect to incident intensity can be calibrated in a relatively straight forward way.

Reticon Array

The reticon array is a one-dimensional array of photodiodes spaced 12-25 μm apart. As many as 2000 elements can be implemented on a single device. The device is periodically scanned and the discharge of each diode produced by optical excitation is digitized by an A/D converter and stored. This gives a one-dimensional

Method	Format	Read Time	Linearity	Dynamic Range	#Elements (0.5")
Film	2-D	10 min.	Nonlinear	10000	10000x10000
Reticon	1-D	33 ms	Linear	1000	500-2000
Vidicon	2-D	1 sec	Nonlinear	200	250x500

Table I.4 Methods of multichannel detection of streak camera output.

readout of the intensity as a function of distance along the array. The reticon array can be fully read out in one scan (33 msec) and has excellent linearity over a wide dynamic range. The one-dimensional format represents somewhat of a restriction for streak camera applications. Two-dimensional reticon arrays are rumored to be under development, but these will not be available for some time.

Vidicon Tube

The two-dimensional alternative to the reticon array is the vidicon system (PAR OMA-II system, for example). In this case the diode array is two-dimensional and is read out by a scanning electron beam in a standard video format. The charge required to recharge each element as the beam scans past it is proportional to the intensity on the diode element. The beam current is monitored as the raster scan progresses, and the two-dimensional image is thus acquired. To gain sensitivity an intensifier section can be added. This version is known as the "SIT-vidicon", or silicon-intensified-target vidicon. A further increase in gain is offered by the "ISIT" model, with two intensifier sections. In the case of detection of streak camera output when the streak camera has a high gain intensifier such as the EMI 4-stage magnetically focused intensifier the singly-intensified version is the best choice. The choice of a two dimensional vidicon recording

system over a one-dimensional reticon system leads to certain compromises. The primary difficulties with the vidicon-based system arise from the electron beam readout of the array. These will be discussed in the next section. For detailed fluorescence kinetics work in small signal regimes and for multi-track detection such as fluorescence polarization and time-resolved spectroscopy the two dimensional format must be adopted.

Summary

These properties are summarized in Table I.4.

I.4.2 Vidicon Intensity Linearity

The recording of optical radiation with a vidicon-based system is not necessarily linear with incident intensity in the case of detection of pulsed signals (Staerk et al. 1982). This arises from the finite resistivity of the target. As the beam scans past a particular diode the time required to recharge the diode is found to depend on the level to which the diode was discharged. Large signals are read out immediately (within a few scans) and small signals may take up to 25 to 30 scans to be fully read out. The main effect of this is that the linearity of response with respect to incident intensity becomes dependent upon the number of scans taken.

Detection of CW and Pulsed Signals

The response of the OMA-SIT system was measured over a wide intensity range using an LED which was pulsed for 100 μ sec to simulate the phosphor decay time of the image intensifier. A green LED was used to provide a spectral distribution similar to the phosphor. Calibrated neutral density filters were placed between the LED and the OMA input face in order to vary the incident intensity in a carefully controlled way. For all conditions investigated the CW response was absolutely linear (slope = 1.0 ± 0.1). For pulsed signals considerable nonlinearity was observed for the case of 5 scan readout. It was found that over the full intensity range the OMA response to incident intensity was superlinear and could be described by a power law. The nonlinearity was characterized by plotting the OMA signal as a function of incident intensity. On a log-log plot the slope of the line yields the exponent. Increasing the number of readout scans to 30 reduces the nonlinearity to an acceptable value of 1.15 ± 0.1 . Increasing the number of scans to achieve an acceptably linear response is not without compromise. The signal to noise ratio begins to decrease noticeably when more than 10 scans are taken. This is because the OMA noise level increases as the square root of the number of scans but the signal increases exponentially toward an asymptotic value as all the charge is read out.

Other methods were tried to reduce the nonlinearity and suppress background levels. One technique involves increasing the readout beam potential from -5 to -8 volts during the readout cycle only. This has the effect of removing the charge efficiently. It was found that this worked in our case also but it could not be implemented in the alternate background subtraction mode because it causes a large thermal spike in the array which builds up a large background error.

Dynamic Range

The dynamic range for pulsed signals with the OMA is in the range of a few hundred. Several factors enter into this. The maximum signal achievable under linear conditions is limited eventually by the A/D converter range (32000 counts per single shot) but in practice this is not obtained without other problems arising. The recording of an intense pulse causes a broadening (flare) and background level increase above the low-level signal background. The minimum signal detectable is the noise level plus any such non-compensatable background shifting.

Cooling of Target

The lag effect which causes nonlinearity problems at room temperature for pulsed signals becomes more severe at low temperature. The operation of the detector at low temperature (-45°C) is desirable because it reduces the dark current level of the array. Also the cooling of the

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Temp. (C)	#Scans	Dwell (μ s)	Mode	V2	Slope (± 0.1)
-45	5	60	Streaking	-5.0	2.3
-45	Realtime	60	CW LED	-5.0	1.0
-45	5	60	100 μ s LED	-5.0	2.4
-45	5	140	100 μ s LED	-5.0	2.0
23	Realtime	60	CW LED	-5.0	1.0
23	30	60	100 μ s LED	-5.0	1.15
23	5	60	100 μ s LED	-5.0	1.40
-45	3	60	100 μ s LED	-8.0	2.0
-45	3	60	Pre-flash	-8.0	2.0

Table I.5 Summary of measured linearity characteristics of SIT-OMA.

preamplifier electronics reduces the electronic noise contribution. The effect of cooling is to give slope of 2.3 (Table I.5). This highly nonlinear intensity response is intolerable. Increasing the number of scans is not sufficient to regain linearity at low temperature when using pulsed signals.

Summary

The linearity characteristics of the OMA are summarized in Table I.5 for all conditions investigated. The best compromise was chosen to be the 20 scan readout at room temperature. This gives acceptable linearity while not seriously affecting signal to noise ratio. This does however limit the overall system repetition rate to about 0.8 Hz.

I.4.3 Background Drift Problem

When acquiring signals with a vidicon-based system it is necessary to subtract the instrumental signal contribution which may be quite sizable. If the background level shifts over the course of the experiment the subtraction of background leads to an offset error which may be positive or negative. In the case of detection of weak signals this can be a serious problem in quantitative work. This also restricts the dynamic range of measurements. In the standard mode of signal averaging the required number of shots is accumulated and stored in memory. The laser trigger is then disabled and the same

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number of background scans is accumulated. The two signals are then subtracted which should result in a correct background removal. In practice the background level drifts in an uncontrollable amount according to the temperature of the array. The background level depends on the array temperature (it doubles for every 7°C rise) and the array is not accurately temperature stabilized. This problem becomes worse as the number of shots averaged is increased because the time interval is longer between the recording of signal and background. A solution to this problem has been found. The method involves alternately acquiring a shot, disabling the laser trigger, and subtracting a background scan.

I.4.4 Alternate Background Subtraction

The method of alternate background subtraction is not implemented on the commercial OMA-II system (Princeton Applied Research Inc.). Using an "open system" software package which was supplied by PAR to LLE in 1977 we wrote FORTH software on the OMA (an LSI-11 based machine) for data reduction and acquisition which was not available from PAR. The method of alternate background subtraction was developed in this thesis to eliminate the background drift problem discussed in the previous section. A block diagram for acquiring data with alternate background subtraction is shown in Figure I.11. This is implemented without hardware modification on the OMA-II 1216 head

Figure I.11 Procedure for signal averaging with alternate background subtraction.

controller by using the relay contact "DC relay #1" in series with the "Experiment Start" output of the OMA to enable/disable the laser trigger signal (Appendix II). The relay actuation is controlled under software command. In order to maintain a laser repetition rate of about one shot per second the acquisition routine must run at 2 Hz. In order to accomplish this the data moving and accumulation routines had to be written in assembly language. In this mode there is no random background drift because the temperature of the array is forced into a regular pattern and long-time fluctuations are quite effectively cancelled (Knox and Forsley 1983). This is exactly the principal of operation of the lock-in amplifier.

I.5 Calibrations

I.5.1 Timing Accuracy

The timing accuracy of the jitter-free streak camera system is limited by the stability of the pulses generated by the Nd³⁺:YAG system. In order to measure the stability of the time origin a differential technique was required because the timing stability is in the range of one picosecond, or much less than the pulse width (30 ps). Figure I.12 shows the result of accumulating 50 shots, storing, and accumulating another 50 shots without introducing any time delays into the beamline. The recorded profile is very stable as evidenced by the

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Figure I.12 System timing stability measurement. A system stability of ± 0.5 ps between sets of 50 shot averages is obtained.

similarity of the two curves in I.12a. In order to determine the shift between the two curves they are subtracted (I.12b). On a ten times magnified scale (I.12c) the difference shows a suggestive form. For small shifts the difference signal can be estimated :

$$I(t+\Delta t) - I(t) \cong \left[\frac{dI}{dt} \right] \cdot \Delta t, \quad (I.5)$$

where $I(t)$ is the unshifted signal and Δt is the shift. Therefore, the difference signal is approximately the derivative of the signal times the shift Δt , so the magnitude of the difference signal is proportional to the shift. In this case the shift Δt is 0.50 ± 0.05 ps. When this measurement was repeated the shift was found to be an average of ± 0.5 ps which is thus the intrinsic timing stability of the system for sets of 50 shot averages. The single-shot error in timing is the square root of 50 times as large as this, or a few picoseconds. The absolute timing of the streak camera also depends on the stability of the 20 kilovolt acceleration supply.

I.5.2 Time Calibration

The sweep speed calibration can be done two different ways with a jitter-free streak camera. The basic idea is to provide the streak camera with two or more pulses separated by an accurately known time delay. Once these have been recorded the distance between the pulses

measured in OMA channels (0-500) represents the time interval specified by the pulse separation time.

Etalon Technique

Using an accurately parallel glass plate of known thickness and index of refraction which has been coated on both sides with a coating of reflectivity r a series of pulses is generated with amplitude dropping by r^2 from pulse to pulse. The number of OMA channels between the recorded pulses gives the sweep speed calibration.

Local Calibration

A local sweep speed calibration can be obtained in a simple way with a jitter-free streak camera by accumulating a number of shots at $t=0$, moving the time delay to a new setting and accumulating a new set of shots.

I.5.3 Sweep Linearity

The form of the deflection as a function of time was measured by averaging 10 shots at each delay setting and recording the center position of the pulse with a reduced sweep bias setting. By applying a reduced bias to the switch it is possible to measure the entire sweep from the undeflected position to the maximum position. The result of this measurement is shown in Figure I.13. The sweep is quite linear over about one nanosecond in this case. The absence of significant ringing is a very important point. One of the major difficulties with conventional drivers is

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Figure I.13 Measurement of deflection function of DC biased GaAs:Cr driver with 300 ohm limiting resistance.

the ringing after the sweep which causes retracing and inaccurate recording of long lifetime transients. In this case a 300 ohm resistor was used as the sweep current limiter.

I.5.4 Sweep Generation Modeling

Initially it was difficult to understand how such a simple deflection driver circuit could produce such a clean linear ramp pulse with high efficiency. The explanation for this behavior has been found in a modeling of the sweep generation circuit as a simple RLC circuit (Figure I.14). The differential equation governing the voltage across the deflection plates is (Knox et al. 1983):

$$L(\ddot{V} + C(R(t) + R_0)\dot{V} + V - V_0 = 0, \quad (\text{I.6})$$

where L is the circuit inductance, C is the deflection plate capacitance, R_0 is the current limiting resistor resistance, V is the voltage across the deflection plates, V_0 is the bias voltage, and $R(t)$ is the time-varying resistance of the gap. The gap resistance can be described as an exponentially rising function after the laser pulse turns off :

$$R(t) = R_{\min} \exp(t/\tau_r), \quad (\text{I.7})$$

E1949

Figure I.14 RLC model of the DC biased GaAs:Cr room temperature deflection driver. The gap is represented as a time-varying resistance.

4) where $R_{\min}$ is the minimum resistance of the gap which is attained after the laser pulse impinges and τ_r is the recombination time. This expression is valid because the sweep risetime is much longer than the pulsewidth, so the resistance may be assumed to start immediately from the minimum resistance $R_{\min}$.

These equations are solved numerically for several cases of experimental interest. In Figure I.15 the solution $V(t)$ is shown for (a) various values of the sweep current limiter R_0 , (b) various values of the minimum resistance $R_{\min}$, and (c) various values of the sweep current limiting resistance R_0 in the case of reduced inductance. An inductance of 32 nH is used for (a) and (b) and a recombination time of 1.5 ns is assumed in all three cases. A DC bias of 2 kV is assumed. In (a) the effect of the current limiting resistor on the rise time of the deflection voltage is shown. With resistances below about 50 ohms the peak voltage exceeds the supply voltage. This is a characteristic of RLC circuits with high Q. If the resistance value exceeds about 50 ohms the peak deflection drops below the bias voltage because the RC response time becomes longer than the recombination time. In (b) the effect of varying the optical energy absorbed by the switch is shown. For minimum resistances greater than about 50 ohms the voltage and hence the peak deflection varies linearly with the optical energy. This

E1995

Figure I.15 Calculated deflection functions $V(t)$ under several conditions (see text).

would lead to sweep speed fluctuations in direct proportion to the amplitude fluctuation of the laser energy. For the cases of $R_{\min}=3$ ohms and $R_{\min}=1$ ohm, representing a three-fold change in optical energy, the peak voltage changes by less than 10%, indicating a saturation behavior. This is the same as found with the charge-line configuration discussed in Section I.2. In (c) the circuit inductance is lowered to 1 nH, resulting in a much faster sweep rise time. This can be achieved in practice by minimizing the length of the connections from the charge source to the switch and deflection plates. Using a GEAR streak camera (ITT) tube and a planar low inductance source (Knox 1981) sweep risetimes down to 375 ps were obtained with a GaAs:Cr switch (Figure I.16).

This analysis suggests that by adding inductance the sweep risetime can be made longer, even up to 5 to 10 ns in a simple way. In practice inductance cannot be added without adding stray capacitance and losses so it is very difficult to obtain a clean deflection ramp in this way. This problem could be solved fairly straight forwardly by a careful engineering study.

I.5.5 Field Intensity Response Uniformity

The response of the streak camera and intensifier system is not very uniform across the field. Several factors contribute to this problem. The pincushion distortion in the OMA causes an intensity dropoff toward

Figure I.16 Measurement of deflection function of GEAR low inductance streak camera driven by DC biased GaAs:Cr switch at room temperature with low inductance source.

the edges of the field, the "S" shaped distortion of the intensifier produces another complicated response function, and the lenses throughout the system contribute to field nonuniformity through $\cos^4$ law. The most severe problem is apparently introduced by the image-converter tube itself. It produces a vignetting on the late-time end of the sweep the onset point of which depends on the setting of the offset adjustment. This can be relatively easily calibrated out by replacing the sample under study with one which has a fluorescence decay time which is long compared to the sweep time window in use. There are several ways to do this. The easiest is to use a dilute solution of rhodamine 6G laser dye in water, a dye with a fluorescence decay time of about 7 ns. This gives a signal which is constant to within less than 10% over the sweep time of 500 ps. Another method is to use the fluorescence of the actual sample under study for the correction if the decay time is known to be long. In the use of both methods the time origin is moved early by about 500 ps to ensure that the rise of fluorescence has been completed before the fluorescence enters the sweep window. In Figure I.17 a measurement of the field response is shown. In this case 300 shots of fluorescence of O_2^- in KCl were accumulated with the time origin set to -500 ps. The dropoff at late times

Figure I.17 Measurement of system field intensity response uniformity function.

is from the image converter tube. The correction function is implemented by smoothing this curve (Figure I.17b) and dividing by it. This results in consistent, accurate correction of the field intensity nonuniformity. The calibration curves obtained in this way compare very well with those taken with a dye solution, as expected.

I.5.6 Sweep Retrace Function

The sweep retrace function describes the motion of the electron beam in the image converter tube after the initial deflection of the beam from off screen at early times to off screen at late times. In the case of fluorescence studies where decay times are much less than the retrace time there is no recording of the signal during retrace. Similarly if the fluorescence decay time is much larger than the retrace time there will be little recording of the signal during retrace. If the fluorescence decay time is comparable to the retrace time the signal will be recorded in the same way as the picosecond signal was recorded and the OMA will display the sum of the two transients such as in Figure 2.10 in the measurement of the fluorescence rise of KBr:Tl^+ .

The sweep retrace function in the jitter-free streak camera is determined by the termination resistance and the capacitance of the image-converter tube. A measurement of the retrace function was made by placing an LED (light emitting diode) in the position of the sample holder so

E2029

Figure I.18 Measurement of sweep retrace function.

that it is imaged by the lens onto the photocathode in the same manner as a fluorescence signal is. The LED is fired by a pulse from an electronic pulse generator with a 10 volt pulse of about one microsecond duration. By varying the time delay between the LED pulse and the laser trigger the retracing function is measured by recording the position of the LED in the in the OMA field. Figure I.18 shows the result of this measurement. The retrace function exhibits a two-component exponential decay, the first with a decay time of 50 microseconds and the second with a decay time of 300 microseconds. The first results from the 4.7 megohm termination resistor and the second may be from a residual long recombination time in the GaAs:Cr switch or from heating.

I.5.7 Sweep Speed as a Function of Bias

The sweep speed is in principle linearly related to the bias voltage applied to the sweep circuit. In practice the high termination resistance used to obtain long retrace times forms a voltage divider with the switch and the sweep speed is not quite linear with bias above 1.5 kV (Figure I.19). This is consistent with the onset of heating of the switch as shown in Figure I.7. The sweep speed is frequently referred to in terms of reciprocal speed or ps/mm. This is convenient for streak cameras when estimating time resolution and sweep time window. Sweep speed of up to 6 ps/mm or half the speed of

Figure I.19 Measurement of sweep speed as a function of DC bias on GaAs:Cr switch. The sweep parameter at 3 kV bias is 10 ps/mm. Sweep parameters of up to 6 ps/mm can be achieved.

light, can be obtained with of bias of 6 kV on a 10 mm GaAs:Cr switch.

I.6 Space Charge Effects

The current density in a typical streak camera in use may be as high as tens of amps per cm^2 . A dynamical spreading of the electron packet is expected because of the internal field of the electron packet when such a high current density is propagated with a picosecond envelope, as discussed previously. The effect of this on streak camera operation is to broaden the time profile of the measured signal in an intensity-dependent manner.

I.6.1 Experimental Results

The broadening of the measured laser pulse was measured for various intensities with the 30 ps second harmonic pulses. Figure I.20 shows the result of increasing intensity on the shape and width of the pulse. The width and shape clearly depend on the intensity in a definite manner. The dynamic range of the streak camera is defined through the pulsewidth scaling with intensity. The dynamic range is defined as the intensity at which the pulse broadens by 20% divided by the minimum detectable signal (the noise level). These measurements agree well with previous measurements for Photochron-II streak cameras (Friedman et al. 1976). For the present system a linear dynamic range of 100 is estimated.

Figure I.20 Space-charge broadening in excitation pulse measurement.

I.7 Signal Averaging

Signal averaging is essential for detailed streak camera measurement of fluorescence. As discussed in the previous section the streak camera has a limit to the amount of signal that can be properly recorded in a single shot. With a jitter-free streak camera system signal averaging can be done in a simple manner without compensation for shot-to-shot fluctuation in the time origin of the data. The most obvious method of repetitively acquiring and averaging signals is to sum them in an accumulator file, as discussed in Section I.4. This results in an increase in signal to noise ratio in proportion to the square root of the number of shots averaged.

I.7.1 Signal to Noise Ratio Improvement

The improvement in signal to noise ratio with averaging many shots is illustrated in a typical case in Figure I.21. Here, weak UV fluorescence of O_2^- in KBr is displayed with (a) one, (b) thirty, and (c) 300 shots accumulated. With the present system the 300 shot series represents a practical limit to the number of shots averaged since at one shot per second it takes five minutes to complete a run. Although in principle the signal-to-noise ratio continues to increase with the number of shots averaged even a 1000 shot series would result in only a 1.7 times further increase in

Figure I.21 Signal-to-noise ratio improvement with signal averaging in a typical weak signal case.

signal-to-noise ratio and require 15 minutes to complete. Operation at a higher repetition rate would of course result in higher data acquisition rates but the problem of lag in the OMA would have to be dealt with. At high enough repetition rates (greater than 10 Hz) the OMA could be read out in continuous scan mode and better linearity could result. At ten Hz thousands of shots could be routinely averaged. This is discussed in Chapter 4.

I.7.2 Photon Counting Technique

In the case of detection of very weak signals the streak camera can be used to detect single photoelectron events. With a high gain intensifier such as the EMI four-stage magnetically focused intensifier the gain can be high enough to allow the recording of signals in the intensity limit of several events per 500 picoseconds. This situation is illustrated in Figure I.21a where the single shot signals are composed of sharp focusing-limited spikes. This is still a case of reasonable signal with about 40 to 50 events per shot. At still lower signal levels the frequency of occurrence is lowered until the events are well separated and individually recorded. In this limit the streak camera can be regarded as a photon counting system with time resolution in the single picosecond range. In Figure I.22 detection in the limit of very weak signals is shown. A weak solution of crystal

Figure I.22 Signal averaging in the single-photoelectron regime.

violet dye was excited with a heavily attenuated laser pulse and the fluorescence was further attenuated to give a weak signal. The intensifier was operated at 35 kV which produces a gain of about 10^7 . Figure I.22a shows a typical shot under these conditions. The accumulation of one hundred shots (b) under these conditions results in greatly improved signal-to-noise ratio as before. The statistics of the single events are analyzed by forming a histogram of frequency of occurrence of events of a certain height within a bin size of 10 counts. This histogram (Figure I.23) was formed from data from six successive laser shots. It exhibits primarily a large peak around 70 counts amplitude with a FWHM of about 50 counts. There are occurrences of much larger events at up to 500 counts, or seven times the size of the predominant event size. The origin of this large spread in signal size is uncertain at this time but it has been suggested that it is from either the statistics of electron multiplication in the intensifier section or in the gain statistics of the image converter tube. This is not well understood at this time and further experiments will have to be carried out to further answer this question.

In any case, one attempt was made to treat the single events as representative of single photoelectron events by invoking a threshold criterion during the acquisition cycle. The procedure involved acquiring a single shot

Figure I.23 Amplitude histogram in single photoelectron regime.

such as in Figure I.22a and recording only those intensities above the threshold level as equal to the threshold level and all those below as zero. The result of an application of this to a typical single shot is shown in Figure I.22c. The averaging operation then proceeded by accumulating the thresholded data instead of the raw data as in the usual procedure. The result of a 100 shot average of the thresholded data shown in Figure I.22d. This was taken under absolutely identical conditions as in Figure I.22b. For this set the threshold was set to 500 counts. The most striking aspect of this result is that the signal-to-noise ratio is effectively unchanged compared to the case of accumulating the raw data. With a threshold value of 500 counts, virtually all the signal is discarded, as can be seen from the histogram (Figure I.23). Over 90% of the occurrences are below 500 counts amplitude. The tentative explanation for this is that all the system noise (OMA digitizing noise and intensifier noise) is rejected before each accumulating operation. The only noise left in the signal is the noise of the signal itself, or the shot noise. One obvious question to ask at this point is the following : "If in discarding over 90% of the signal the same signal-to-noise ratio results, is there a better way to handle this 90% of the signal which could result in a higher signal-to-noise ratio than the simple accumulation ? It seems plausible

that in this regime of operation the simple accumulation is not the best averaging technique.

APPENDIX II EXPERIMENTAL TECHNIQUES

II.1 Sample Preparation

Samples of alkali-halide crystals doped with various fluorescent impurities were prepared in a variety of ways. These will be briefly described.

II.1.1 Crystal Growing

Crystals were grown using the Czochralski method. A seed crystal of the same material as the desired crystal was mounted on a cooled copper rod and the seed was slowly pulled from the melt (about 5 mm per hr). The melt temperature was regulated to within about one degree by a temperature controlled oven with the temperature sensor in contact with the alumina crucible. The seed crystal was rotated at about one revolution per minute. It proved impossible to grow good single crystals with this system but reasonable boules of size 1/2" round by 1" long could be grown consisting of several crystals. Crystals of KCl, KBr, NaCl, RbI and KI were grown with this technique. Pure crystals of LiF and NaF and crystals of KBr:Tl⁺ were obtained from Harshaw, Inc. Single crystal NaNO₂ was obtained from Dr. Ishibashi from Nagoya University, and

some crystals of $KI:O_2^-$ were obtained from H. Labbe at NRC in Canada.

II.1.2 Doping Into Melt

The most reliable method of doping alkali halide crystals is to add some impurity into the melt prior to growing the crystal. Excellent samples of $KCl:O_2^-$ and $KBr:O_2^-$ were produced by adding 0.5% by weight KO_2 to the melt. Although other researchers grew the crystals in a pure oxygen atmosphere, we obtained good concentration of O_2^- with no special atmospheric controls. The addition of impurity to the melt can severely change the growth properties of the crystal. For KCl and KBr doping at the level of 0.5% produced no serious interference, but for RbI and KI it was not possible to grow crystals at this doping level. At a doping level of 0.05% KO_2 good KI and RbI crystals were grown but the concentration of O_2^- was low.

II.1.3 High Temperature Gas Doping

Two other techniques of preparing molecular ion centers were tried. The first involved sealing the proper crystals in quartz ampoules under vacuum with a small quantity (several mg) of sulphur or selenium for production of S_2^- or Se_2^- centers, respectively. This procedure worked well but poor picosecond fluorescence results were obtained because of low quantum efficiency of these centers. The second technique was used for O_2^-

doping. Samples were placed in a long quartz tube inside an oven. Oxygen gas was flowed over the samples at a temperature close to their melting temperature (typically 20 degrees C below melting) for a period of up to 200 hours. This resulted in the creation of O_2^- centers in the crystal KI.

II.1.4 High Energy Radiation Exposure

The irradiation of alkali halide crystals with high energy radiation creates color centers through several mechanisms. The color centers studied in this thesis were M centers in LiF and NaF. These M centers are the only centers that emit in the detection range of the streak camera with an S-20 photocathode. The various methods used for the production of these centers will be briefly discussed.

X-rays

A stream of X-rays from a conventional X-ray tube operating at 50 kV at a current of about 20 mA is capable of coloring samples to an F-center density of about 10^{17}cm^{-3} in a time of about 2-4 hours. Samples colored at room temperature in this way exhibit a reasonable concentration of M and R centers (F_2 and F_3 centers). The coloration is not very uniform but it is quite adequate for the purpose of these experiments. The Institute of Optics X-ray machine was used for this coloration.

Gamma Rays

Gamma rays are very effective in producing color centers in alkali-halide crystals. Their large penetration depth produces a very uniform coloration. A good proportion of M and R centers is produced in this manner also. A cobalt-60 source of 6.5 MeV gamma rays at the Strong Memorial Hospital was used for this coloration.

MeV Protons

The stopping range for 1.5 MeV protons in alkali halides is about 50 microns. When irradiated with a 1.5 MeV beam of protons for a period of two hours crystals of LiF and NaF showed good coloration (absorption of O.D. 1.5 in the F-band) with a small penetration depth. The fluorescence properties of these centers were not measured. The irradiation of the crystals was performed by L.B.Knox at the SUNY Geneseo Physics Department.

II.2 Cryogenics

A closed-cycle helium recirculator cryogenic system (CTI Cryogenics model number 21) was used to maintain samples at cryogenic temperatures. A sample could be cooled from room temperature to cryogenic temperature in about 30 minutes. The temperature of the sample holder was regulated at the base of the cold finger where the sample holder was attached. This gave regulation to within about one degree.

(X4)

II.2.1 Sample Mounting

The samples of alkali halide crystals were clamped in a gold-plated copper ring which was attached to the cold head. The samples were usually held in place with indium foil and a silicone O-ring.

II.3 Laser System

II.3.1 System Description

The laser system which was built and characterized for this work is shown in Figure II.1. It consists of an Active-passive modelocked Nd³⁺:YAG laser (Seka and Bunkenburg 1978), a high-contrast single pulse selection system and a single stage of amplification. The system produces single pulses at 1064 nm with energy of one mJ, pulsewidth of 35 ps with shot-to-shot fluctuations of $\pm 10\%$ and $\pm 5\%$ respectively and energy contrast of 10^5 at a repetition rate of up to 2 Hz. The active modelocking element (Quantronix Acousto-optic modelocker unit) enables the production of highly reproducible pulse trains of $\pm 2\%$ shot-to-shot peak fluctuation. By carefully controlling the temperature of the modelocking crystal with a circulating cooling system (Thermomix model 1420) at $25^\circ\text{C} \pm 0.1^\circ\text{C}$ excellent long term stability has been achieved. The system typically operates for 4-5 weeks before requiring maintenance. The Q-switch/modelocking dye (EK 9740 in 1-2-Dichloroethane) is flowed through a wedged 200 μm cell. The switchout system consists of a krytron high

Figure II.1 Active-passive modelocked oscillator, switchout system and amplifier configuration.

voltage pulser (4.5 kv peak, 1 ns rise and fall times, 6 ns FWHM) driven by an avalanche stack. The avalanche stack is triggered by a discriminator which monitors the rejected train from the first polarizer. A double-Pockels cell configuration with series electrical transmission is employed with high rejection Glan-Thompson polarizers to obtain the high optical contrast which is required for jitter-free operation of the streak camera. A single stage of amplification operating at a single pass gain of about 5 provides a final energy of about 1 mJ in the single pulse. RF for the modelocker (50 MHz) is derived from the LC oscillator section of a Quantronix modelocker driver unit via the reference output. The signal is passed through a variable attenuator string to adjust the RF power and into an ENI 20 watt RF amplifier. Best operation is obtained when the crystal is operated off resonance with 2.5 W incident and 0.4 W reflected power, as monitored by an in-line RF power meter.

Two helium-neon lasers provide CW visible beams for alignment. Power conditioning for the two 1/4" YAG rods is provided by a Raytheon oscillator supply which is simmered and ignitron-triggered and a custom-built amplifier supply. The primary source of shot-to-shot single pulse energy instability in this system ($\pm 10\%$) is the switchout system krytron. Shot-to-shot stability of

+2% should be obtained with a better switchout system if a better one is ever available.

II.3.2 Excitation Wavelengths

One convenient feature of this laser system for general scientific work is the availability of high power (MW) pulses which allows for a variety of nonlinear wavelength conversion schemes. These will be briefly described in this section. Table II.1 summarizes the techniques which have been used here to obtain different excitation wavelengths to date. Several other techniques could be implemented such as parametric oscillators but these techniques may require more optical energy than is available in this system.

Harmonic Generation

The most straightforward wavelength conversion technique is harmonic generation. The second, third and fourth harmonics are readily generated with energies of 30, 5 and 3 microjoules, respectively. These figures are not optimal but are typically obtained with angle tuned doubler and tripler and a temperature tuned quadrupler.

Stimulated Raman Scattering

Using SRS in liquids a variety of other wavelengths are available with sufficient quality for excitation of fluorescence. Acetone provides two stokes lines and one antistokes line when pumped by the second harmonic (532 nm). In benzene the Raman shift is smaller and several

Technique	Material	Pump (nm)	Wavelengths (nm)		
=====					
Harmonic Gen.	KD*P	1064	532	355	266
SRS	Acetone	532	729	615	467
SRS	Benzene	532	633	595	561
Short-Cav. Dye	R6G/R640	532	580-650		
SRS + Doubling	Acetone+LiNbO3	532	307		
=====					

Table II.1 Nonlinear wavelength conversion schemes.

stokes orders are readily obtained. The desired excitation wavelength is selected with an interference filter. Since the SRS process is highly nonlinear we might expect some jitter between the excitation pulse which also drives the streak camera and the stokes and antistokes stimulated pulses. In practice jitter of only about 5 ps is introduced by this effect.

Short Cavity Dye Laser

A thin (200 μm) wedge of high concentration (10^{-3}M) laser dye can be effectively used to obtain pulses at other wavelengths. When pumped by the second harmonic pulse a R6G wedge emits pulses (essentially single-pass ASE) of 10-25 ps width depending on how far above threshold the dye is pumped (Knox 1980). This broadband light (about 4-5 nm) can be coarsely tuned by changing the solvent or dye.

Combination of SRS and Harmonic Generation

Wavelengths in the range of 290 to 310 nm can be obtained by doubling the SRS light. In one case the 615 nm first stokes line of acetone was doubled in a 2 mm LiNbO_3 crystal to yield about a microjoule of excitation at 307 nm. Other stokes lines could be used for this.

II.4 System Configuration

The synchronization of the OMA scanning with the laser firing is accomplished in a way which allows for automatic alternate background subtraction. Figure II.2

shows the system layout. A Princeton Applied Research Optical Multichannel Analyzer (OMA) system is employed. The 1216 (head controller) initiates a scan of the OMA head (1254), at the same time sending out a signal from the "Exp. Start" connector. This signal is passed through DC relay #1 (RY1) and enters an optoisolator. The optoisolator triggers an HP pulse generator which fires the laser. The pulse generator also serves as a clock when not acquiring data. For a background acquisition the relay RY1 is opened and the scan is initiated, without the laser being fired. This results in the acquisition of a background signal.

For streak camera operation at gain of over 25 kV on the EMI intensifier the OMA must be operated in gated mode for background suppression. This requires a -1100 volt pulse for the first intensifier which is synchronized to the laser and slightly longer than the phosphorescence decay of the intensifier phosphor screen (300 μ s). A PAR model 1211 pulse is used for this with a 900 usec pulsewidth. The trigger for this unit is derived from a silicon switch ("T" in Figure II.1) which is biased at 9 volts and excited by the full rejected train from the second polarizer of the switchout system. This provides a reliable hard trigger for the gating unit. For signaling the operator after a data acquisition cycle an audio alarm

Figure II.2 Overall system configuration.

("S") is connected to DC relay #2 and the relay is activated after the acquisition.

II.5 Time Origin Determination

II.5.1 Importance of Time Origin

In measurement of fluorescence response times which are comparable to the width of the excitation pulse in use (in this case 25 ps) the absolute timing capability of the jitter-free streak camera is very important. In these cases is it possible to make a one-parameter fit to the data without using the time origin as an arbitrary fitting parameter. This leads to increased measurement accuracy and reliability. Although the jitter-free streak camera has the intrinsic capability to make a series of measurements with absolute time correspondence of 1 ps with respect to each other it is not in general a trivial matter to properly make fluorescence measurements with respect to an excitation pulse with absolute time correspondence of 1 ps. The reasons for this will be discussed in this section.

II.5.2 Methods of Absolute $t=0$ Measurement

Several methods of determining the absolute $t=0$ of excitation have been tested for the case of color centers in alkali halides which have VR times of less than 1 ps.

Dye Comparison

By replacing the sample under study with a dye cell an absolute $t=0$ can be determined. The VR time of the laser dye rhodamine 6G has been investigated by an optical kerr gating technique (Mourou and Malley 1975). In this measurement the risetime was not resolved and an upper limit of 2 ps was determined. Thus such a laser dye could be used to represent an instantaneous response to the excitation pulse under conditions which are identical to the sample under study. While this method should work in principle, in practice several error sources enter which make this technique inaccurate and unreliable with timing errors of up to 10 ps. The main advantage of using the dye reference is that the fluorescence wavelength of the dye can be somewhat matched to the fluorescence wavelength under study and wavelength-dependent timing errors can be effectively cancelled. Although the color centers and molecular ions studied in this thesis exhibit a large stokes shift between the excitation wavelength and the fluorescence wavelength the timing errors introduced by replacing the crystal with a dye cell are much larger than the wavelength dependent errors.

Scattering Cell

The use of a scattering cell for a $t=0$ measurement is standard in picosecond spectroscopy. In the case of these measurements it provides a scattered signal at the excitation wavelength with an origin in the bulk of the

specimen. This feature is attractive since in the case of a weak absorption where the absorption depth is greater than the sample thickness the fluorescence signal emanates from the bulk. The main problem with the use of a scattering cell is the same as that of the dye cell: the necessary glass window for containing the solution causes a scattered signal and light piping which destroys the absolute $t=0$ measurement.

Direct Scatter

The measurement of the absolute $t=0$ directly from the surface scatter can be the most accurate one of these methods, but it must be applied with care. Alkali halides are typically highly transparent and low scattering crystals. Thus most of the scattered signal comes from the front and back surfaces (Figure II.3). Since the fluorescence signal comes from the bulk the impulse response function for the scattering measurement is different from that for the fluorescence measurement.

II.5.3 Error Sources

The largest errors in timing between the scattered signal and the fluorescence signal result from finite sample thickness. It is surprising that these errors are as large as they are. These results will also apply to experiments in chemistry and biology in the case of weakly scattering samples in 90° excitation geometry.

Figure II.3 Geometry for 90° fluorescence detection and surface scattering origin.

Finite Sample Thickness

The time delay between the arrival of the front and back surface scattered pulses is given by:

$$\Delta = \frac{d}{c} \left[\frac{(n - \cos^2 \theta / n)}{(1 + \cos^2 \theta / n^2)^{1/2}} + \frac{(n - \sin^2 \theta / n)}{(1 - \sin^2 \theta / n^2)^{1/2}} \right], \quad (\text{II.1})$$

where d is the sample thickness, c is the speed of light, n is the crystal index of refraction, θ is the incidence angle and Δ is the time delay. This is a slowly varying function of incidence angle, as shown in Figure II.4. A thickness of 1 mm is assumed and the time delay is plotted for (a) $n=1.61$, (b) $n=1.48$ and (c) $n=1.32$, corresponding to RbI, KCl and NaF, respectively. Timing errors as large as 9-10 ps can be encountered with just a 1 mm thick crystal. Thus we can write for the scattering impulse response function :

$$F_{\text{SCATT}}(t) = s_1 \delta(t - \Delta/2) + s_2 \delta(t + \Delta/2), \quad (\text{II.2})$$

where s_1 and s_2 are the relative scattering coefficients for the front and back surface, respectively. For the fluorescence response function :

$$F_{\text{FLUOR}}(t) = s_0 \text{rect}(t; \Delta), \quad (\text{II.3})$$

representing a rectangular function in time with width Δ at $t=0$ and strength of s_0 . In order to determine the

Figure II.4 Time delay between front and back surface scattered signals as a function of incidence angle and index of refraction of crystal for a thickness of 1 mm.

influence of this on a typical fluorescence measurement with 25 ps pulses the following quantities are computed:

$$I_{\text{SCATT}}(t) = I_{\text{EXC}}(t) \otimes F_{\text{SCATT}}(t) \quad (\text{II.4})$$

$$I_{\text{FLUOR}}(t) = \left[I_{\text{EXC}}(t) \otimes F_{\text{FLUOR}}(t) \right] \otimes F_{\text{3-LEVEL}}(t), \quad (\text{II.5})$$

x₁ where $I_{\text{exc}}(t)$ is the excitation pulse time variation assumed to be gaussian with a width of 25 ps and $F_{\text{3-level}}$ is the response function of the three-level system. The relative sizes of s_1 and s_2 determine the symmetry of the measured scattered excitation pulse. It is clear that for a given crystal even a small surface feature such as a scratch can play a large part in the $t=0$ measurement. Simply moving the crystal slightly can change the measured excitation pulse shape and position. In Figure II.5 this situation is illustrated with $\Delta = 22$ ps (a 2 mm KCl crystal). First the scattered excitation signal is calculated for the cases of unequal surface scattering (a) $s_1=10$ and $s_2=3$, and (c) $s_1=3$ and $s_2=10$. This demonstrates how an asymmetric pulse may be measured. In (b) the fluorescence driving function is calculated (that is, the excitation pulse convolved with the rectangle function) under these conditions. In (d) and (e) the extreme cases of $s_1=10$, $s_2=0$ and $s_1=0$, $s_2=10$ are shown with the calculated three-level fluorescence rise driven by the

Figure II.5 Effect of finite sample thickness in fluorescence timing measurements.

broadened excitation pulse (b) for the case of a fast risetime ($\tau=0$). Thus the timing error can be as large as $\Delta/2$ between the scattered excitation pulse and the 50% rise point of the fluorescence curve in the case of scattering dominated by a single surface. The best remedy for this is to use thin samples (less than 0.5 mm). Crystals with some bulk scattering give very reliable $t=0$ measurements compared to highly scatter-free crystals. In the case of the NaF:M experiment a crystal of 300 μm thickness was used. The use of a very thin crystal will result in the loss of signal for the case of weak absorption. In any case the crystal should be cleaved as carefully as possible in order to minimize s_1 and s_2 and hence take advantage of any bulk scattering which is available.

Wavelength Dependent Errors

There are two sources of wavelength dependent errors in absolute timing comparisons of excitation pulses and fluorescence curves. First and foremost is the dispersion of the collection lens. This error is shown for the case of (a) a six-element double-gauss $f/1.9$ lens and (b) a fused silica lens of thickness 1 cm (Figure II.6). The fused silica lens has a very weak dispersion in the visible but is only used for UV applications because of its poor imaging qualities and lack of chromatic

Figure II.6 Wavelength-dependent timing errors due to collection lens dispersion for (a) $f/1.9$ double Gauss and (b) 1 cm fused silica lens.

aberration correction. For the $f/1.9$ double-gauss lens a typical error is -2.5 ps between 532 and 700 nm.

Second, the initial photoelectron velocity in the streak camera depends somewhat on the energy of the incident photon. The photoelectron spectrum of a semitransparent photocathode is dominated by secondary electrons with a thermal energy distribution. Theories of this effect are not well developed. In the case of secondary electron emission an Einstein model for the initial electron velocity is not justified but it may be adopted to estimate the largest value the wavelength-dependent error from this source. In Figure II.7 the relative time of flight of the photoelectrons as a function of energy of the incident photon is shown. This was calculated assuming a two-field model of the image converter tube. For an extraction field of 20 kV/cm as in a Photochron-II image converter tube the time delay is nearly constant over the visible even in this model which overestimates the magnitude of this effect. It is interesting to note that this effect tends to cancel the dispersion-induced effect of the lens, and at lower extraction fields the effect would become pronounced. This effect is actually well known to photon counting spectroscopists because the photocathode to first dynode field in a photomultiplier is much smaller than in the

Figure II.7 Wavelength dependent timing error due to photoelectron velocity changes in the Einstein approximation.

image converter tube and time errors of up to several hundred ps are obtained.

Thus the wavelength dependent absolute timing errors are of the order of several picoseconds for most experiments. In cases where this effect is important the data can be corrected for this effect by simply shifting the excitation and fluorescence functions by the appropriate amount.

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