(1968).

[3] J. P. McTague and G. Birnbaum, Phys. Rev. Lett. 21, 661 (1968), and to be published.

[4] At low pressures of Ar and Kr, the damped rotational Raman spectra of impurities (e.g., N_2) can distort the spectral form at large frequency shifts. For the purity of gas used here (less than 10 ppm impurities) these effects were found to be negligible.

[5] For the data in Fig. 1, the error (including systematic effects) is estimated to be no larger than the random scatter between adjacent points. For further details concerning the background subtraction see R. E. Slusher, C. M. Surko, and J. Strautins, to be published.

[6] L. Silberstein, Phil. Mag. 33, 521 (1917).

[7] A. D. Buckingham and D. A. Dunmur, Trans. Faraday Soc. 64, 1776, (1968).

[8] J. I. Gersten, to be published.

Picosecond Emission Spectroscopy of Homogeneously Broadened, Electronically Excited Molecular States

P. M. Rentzepis, M. R. Topp, and R. P. Jones
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

and

J. Jortner
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(Received 10 November 1970)

We present a direct observation of an ultrafast time-resolved emission spectrum of a dye molecule in solution, the time resolution of the system being 2×10^{-12} sec. Vibrational relaxation within the vibrational manifold of the excited electronic state of rhodamine 6G occurs within 6×10^{-12} sec. We discuss the implications of these results for the understanding of homogeneous broadening of excited electronic states of large molecules.

Inhomogeneous line-broadening effects resulting in the broad optical absorption bands for intravalence electronic excitations of large organic molecules in solution can be attributed to two major sources: (a) intramolecular sequence congestion,[1] (b) intermolecular coupling (via linear and quadratic terms in nuclear displacements) of each molecular vibronic level to the lattice[2] (or rather to the solvent molecules in the nearby environment of the guest molecule). When the molecule is characterized by a significant change in the equilibrium geometry between the two electronic states, then electronic excitation from the ground state will result in a distorted nuclear configuration in the excited electronic state, which subsequently relaxes vibrationally via intramolecular and intermolecular channels. The final result of this relaxation process involves dissipation of vibrational energy to the medium.[3] This relaxation mechanism, which for large molecules is believed to be as fast as the time scale of the spontaneous radiative decay,[4] results in homogeneous line broadening. Until recently, these ultrafast molecular processes were not amenable to experimental study.

The recent development of picosecond pulse techniques[5] and the measurements of the pulse duration by two-[6,7] and three-photon[8,9] fluorescence methods has initiated studies of ultrafast molecular relaxation processes.[10-16] Up to date, time-resolved experimental methods utilized for picosecond spectroscopy have been based upon averaging of several laser shots[16] at each wavelength to display the "average" time-dependent spectrum. In this note we present what we believe to be the first direct observation of an ultrafast time-resolved emission spectrum of a large organic molecule in solution. A method has been developed for monitoring a time-versus-frequency spectrum by a normal spectrometer. The time resolution is limited by the width of the mode-locked laser pulse and by the rotational relaxation time of the optical shutter. With obvious modifications the time resolution of this system can be less than 10^{-12} sec, while the frequency resolution is strictly spectrometer dependent.

The experiment utilizes as a time-resolving element an optical shutter consisting of a 0.1-mm CS_2 liquid cell located between a pair of crossed polarizers.[17,18] The shutter is opened by a picosecond pulse of the first harmonic of a Nd^{+3}-glass mode-locked laser. The shutter ad-

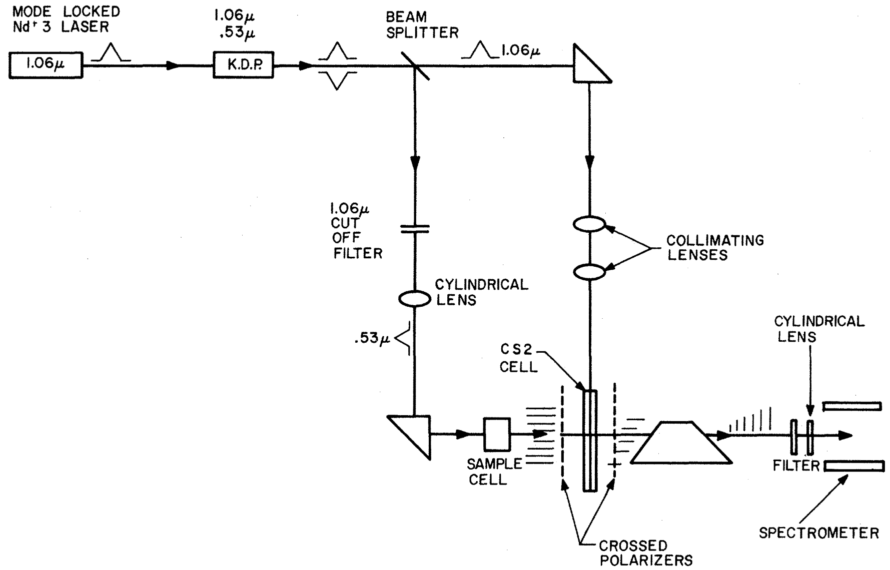

FIG. 1. Experimental arrangement.

mits light through different points along the propagation of the picosecond laser pulse for the time of 1.8 psec which is determined by the rotational relaxation rate of the solvent molecules.[18] We were able to monitor the time dependence of the emission of an organic dye molecule in solution on a total time scale of ~20 psec, with a time resolution of 2 psec. Rhodamine 6G (concentration ~$10^{-4}M$) in ethanol was excited by a picosecond pulse of the second harmonic of a mode-locked Nd^{+3}-glass laser, the resulting emission being fed through the optical shutter into the entrance slit of a spectrograph. The experimental setup is displayed in Fig. 1. The picosecond pulses emitted by a mode-locked Nd^{+3}-glass laser generate the second harmonic in a potassium dihydrogen phosphate crystal. The pulses are separated by two beam splitters and propagate along the paths indicated in Fig. 1. The second harmonic induces the excitation and in the present case induces stimulated emission. This emitted radiation passes through the optical shutter during the time and at the point where the shutter is opened for ~2 psec. The path of the first harmonic along the CS_2 cell provides the time-resolving mechanism. A prism located in front of the spectrometer rotates the emitted beam by 90° thus displaying the time response vertically along the slit and therefore on the plate of the spectrometer (Spex model No. 1500, dispersion 10 Å/mm). The resulting time-versus-wavelength plate is shown in Fig. 2. The second-harmonic (5300 Å) which arrived simultaneously with the shutter-opening pulse is shown to start at $t = 0$. Then there is essentially absence of stimulated emission for the period of ~6 psec (upper limit) before the onset of the stimulated emission from the rhodamine 6G dye which has a duration of ~10 psec.

Using a longer (5-cm) CS_2 cell or substituting for the CS_2 in the optical shutter a liquid characterized by a longer rotational relaxation time (e.g., nitrobenzene), and using a photodiode, we were able to resolve the time response of the normal fluorescence which is characterized by a decay time of ~6 nsec. The reliability of the system was further checked by performing other experiments on known systems[14,15] such as Q-switching dyes.

The method of time-resolved picosecond emission spectroscopy yields a direct measurement

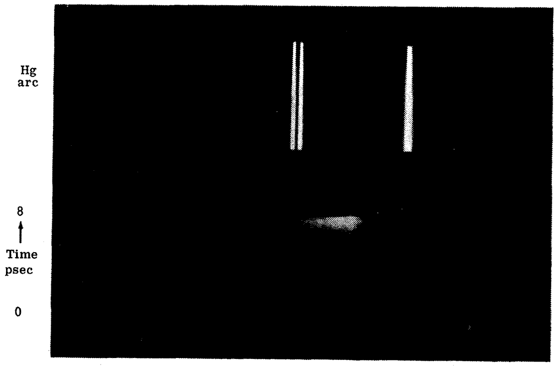

FIG. 2. Photograph of the time-resolved spectrum of rhodamine 6G in ethanol.

of the relaxation mechanism in an excited electronic state of a molecular system. The data reported herein provide the first direct experimental determination of time- and frequency-resolved vibrational relaxation in an excited electronic state of a large molecule.

Recent work on relaxation of the first excited state of the azulene molecule[10] pumped by a mode-locked second harmonic of a neodymium laser monitored simultaneously vibrational relaxation and intersystem crossing (i.e., electronic relaxation), and these two parallel decay channels could not be separated. The present system (rhodamine 6G) is characterized by an emission quantum yield which is close to unity[4] (98%) whereupon the vibrational relaxation channel could be studied. As the stimulated emission from a dye molecule in solution occurs via a four-level mechanism,[4] we can assert that, for rhodamine 6G, vibrational relaxation from the vibrationally energy-rich, electronically excited state, which is accessible by optical excitation, takes place within a period of ~6 psec, which represents the rate of reaching thermal equilibrium within the vibronic manifold of the electronically excited state. Our current theoretical understanding of these relaxation processes is rather meager at present. Two mechanisms which probably operate both simultaneously and consecutively will contribute to the relaxation process studied herein: (a) The intramolecular vibrational energy is redistributed. Intramolecular anharmonic coupling couples the optically active vibrational modes with other molecular vibrational modes, resulting in redistribution of the excess vibrational energy (which remains constant for this process) among all the intramolecular vibrational modes. This mechanism should be operative also in an isolated large molecule in the low-pressure gas phase and is experimentally confirmed[19] by the observation of an identical Stokes shift of large molecules in solution and in the vapor phase. (b) The intramolecular vibrational energy is dissipated. Coupling of the intramolecular vibrational modes to the lattice modes (i.e., the nuclear motion of the nearby solvent molecules) leads to the decay of an intramolecular vibrational mode into "lattice" phonons. Through the intermolecular coupling, described by quadratic terms in nuclear displacements, an intramolecular phonon may be emitted and a medium vibration excited. Anharmonic intermolecular interactions will result in the decay of an intramolecular vibrational mode into a pair of lattice modes. In this context mechanism (a), which leads to the population of low-frequency intramolecular vibrational modes, will provide doorway states for intramolecular vibrational energy dissipation to the medium.

The vibrational relaxation rate studied herein is directly related, via the Fourier transform of the homogeneous broadening contribution, to the width of the absorption bands of the large molecule in solution. Invoking the terminology of time-dependent perturbation theory, the optical transition results in the excitation of virtual vibrational states which, as a consequence of intramolecular and intermolecular coupling, decay to other vibrational states of the supermolecule which consists of the solute and the nearby solvent molecules.

Finally it may be worthwhile to point out that we have observed the stimulated Raman emission from the solvent to be delayed by less than 3 psec relative to the laser pulse, which is consistent with the theoretical arguments that, in the picosecond time domain, molecular vibrations may be excited only in a transient sense.[17,20]

We wish to thank Dr. D. C. Douglass for his helpful comments and criticism.

---

[1] J. P. Byrne and I. G. Ross, Can. J. Chem. 43, 3253 (1965).

[2] M. Lax, J. Chem. Phys. 20, 1752 (1952).

[3] P. Seybold and M. Gouterman, Chem. Rev. 65, 413 (1965).

[4] B. I. Stepanov and A. N. Rubinov, Usp. Fiz. Nauk. 95, 45 (1968) [Sov. Phys. Usp. 11, 304 (1968)].

[5] D. A. Stetser and J. A. DeMaria, Appl. Phys. Lett. 9, 118 (1966).

[6] J. A. Giordmaine, P. M. Rentzepis, S. L. Shapiro, and K. Wecht, Appl. Phys. Lett. 4, 216 (1967).

[7] P. M. Rentzepis and M. A. Duguay, Appl. Phys. Lett. 4, 218 (1967).

[8] P. M. Rentzepis, Bull. Amer. Phys. Soc. 15, 282 (1970).

[9] P. M. Rentzepis, C. J. Mitschele, and A. C. Saxman, Appl. Phys. Lett. 17, 122 (1970).

[10] P. M. Rentzepis, Chem. Phys. Lett. 2, 117 (1968).

[11] P. M. Rentzepis, Chem. Phys. Lett. 3, 717 (1969).

[12] P. M. Rentzepis, Photochem. and Photobiol. 8, 579 (1968).

[13] E. Drent, G. Makkes Van der Deijl, and P. J. Zandstra, Chem. Phys. Lett. 2, 526 (1968).

[14] R. I. Scarlet, J. F. Figueira, and H. Mahr, Appl. Phys. Lett. 13, 71 (1968).

[15] M. M. Malley and P. M. Rentzepis, Chem. Phys. Lett. 3, 534 (1969).

[16] P. M. Rentzepis, Science 69, 239 (1970).

[17] M. M. Malley and P. M. Rentzepis, to be published.

[18] M. A. Duguay and J. W. Hansen, Appl. Phys. Lett. 15, 192 (1969); G. Mayer and F. Gires, C. R. Acad. Sci. 258, 2039 (1964).

[19] D. Eastwood, L. Edwards, M. Gouterman, and J. Steinfeld, J. Mol. Spectrosc. 20, 381 (1966).

[20] L. Carman, M. E. Mack, F. Shimizu, and N. Bloembergen, Phys. Rev. Lett. 23, 1327 (1969).

"Semi-Auger" Processes in L_{23} Emission in Ar and KCl

J. W. Cooper and R. E. LaVilla
National Bureau of Standards, Washington, D. C. 20234
(Received 14 September 1970)

X-ray emission studies in Ar and KCl due to formation of an L_{23} vacancy reveal a low-energy satellite below the main emission peak. Comparison with other data on related processes indicates that this satellite is due to two-electron effects (configuration interaction) in the final state of the emission process.

In this Letter we wish to report direct evidence of a two-electron process in L_{23} emission which corresponds to simultaneous filling of an inner-shell hole and excitation of a valence-shell electron with emission of a single photon. This process, which would produce a low-energy satellite approximately 10 eV below the main L_{23}-M_1 emission peak, has been observed previously[1-3] in K and Cl spectra. While processes of this type have been postulated earlier,[4,5] it has been impossible to demonstrate conclusively that they are in fact occurring in experiments of this type.[1-3] The use of argon gas in our experiment makes it possible to rule out double vacancies in the initial state as an explanation of the observed low-energy spectral feature. It also makes possible a definitive interpretation of the emission results in terms of the known spectroscopic levels of Ar II. Evidence for a similar process in K-shell emission of Al, Si, and S involving two-electron processes in the L_{23} subshell has recently been reported.[6] However, the intensities of these K-shell emission features[6] represented only a small fraction (<1 %) of the parent line, whereas in the L_{23} emission reported here the effects are considerably larger (of the order of 10 % of the parent line).

Emission spectra were obtained using a single-crystal Bragg spectrometer with a Langmuir-Blodgett type lead myristate analyzer. Resolution of the analyzing crystal (~2 eV) is unknown. The resolution as limited by 0.4° Soller slits varied with wavelength from about 1.25 eV (at potassium L_{23}) to about 0.21 eV (at Cl L_{23}). Radiation was detected with a flowing-gas proportional counter followed by conventional electronic data logging, while step-scanning. Excitation was provided via a Pierce-type electron gun operating at 10 kV with a current of 100 mA in the case of argon and 0.05 mA for KCl spectra.[7] For the argon measurements the target atoms consisted of a continuous gas flow through the system. The KCl L_{23} spectra were obtained from a single crystal of KCl attached to a nickel strip with silver conducting epoxy. Ni $L\alpha_{1,2}$ radiation in third through fifth orders and C $K\alpha$ from graphite were used to calibrate the energy scale. Further experimental details will be presented elsewhere.

Emission spectra corresponding to Cl, Ar, and K are shown in Figs. 1(a), 1(b), and 1(c) respectively. The potassium L_{23} emission spectra in Fig. 1(c) is located on the tail of the carbon $K\alpha$ emission which comes from pump oil deposited on the specimen. Figure 1 shows, in addition to an unresolved L_{23} doublet (the large peak), an additional structure lying approximately 6, 11, and 14 eV below the main peak in Cl, Ar, and K, respectively. The separation of the low-energy peak from the main peak in KCl is in agreement with previous measurements.[2,3]

The interpretation of the low-energy peaks in Fig. 1 as a "semi-Auger" process requires that all other possibilities be ruled out. Alternative possibilities include the following: (1) Excitation of L_1 rather than L_{23} may occur followed by an L_1-L_{23},M Coster-Kronig process leading to L_{23} and M vacancies in ions of higher charge. (2) Two-electron excitations may occur in the excitation process, i.e., the formation of L_{23} single vacancies may be accompanied by a fraction of ions in excited or doubly ionized states due to electron "shakeoff."[8]

Both of these possibilities can be ruled out in the case of argon by energetic considerations.

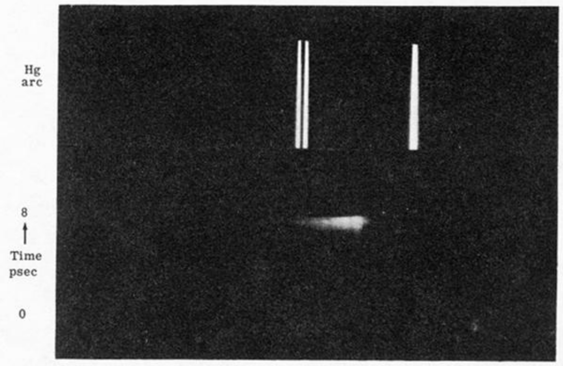

FIG. 2. Photograph of the time-resolved spectrum of rhodamine 6G in ethanol.