moving out of phase with respect to one another.

We have presented here a new technique for investigating the normal-mode structure of an amorphous solid using molecular-dynamics studies. This technique can be used where all conventional techniques of diagonalizing the dynamical matrix no longer work since the matrix is too large and not sparse enough to diagonalize even on modern-day computers. The technique should also be applicable to finding other kinds of eigenfunctions of second-order equations, such as the wave functions of electrons. We have applied the technique to the localization of modes in a Lennard-Jones frozen fluid and found that there is a threshold frequency above which localization occurs. The study of localization by molecular-dynamics techniques is of particular interest since it is a true interacting many-body system. As the amplitude of a mode is increased it interacts more strongly with other modes. The way in which localization affects the interaction of modes has not been previously studied. Simulations of electron localization[7] do not offer the possibility of studying this kind of phenomena. We are currently pursuing the studies of our localized modes as a function of amplitude in order to understand how mode-mode interactions affect their properties.

This work was supported in part by National Science Foundation Grants No. DMR 80-21256 and No. DMR 80-17756 and by the U. S. Department of Energy. S. R. N. benefited from an Alfred P. Sloan Foundation Fellowship.

---

[a] Present address: Exxon Research and Engineering Company, Linden, N. J. 07036.

[1] G. S. Grest, S. R. Nagel, and A. Rahman, Solid State Commun. 36, 875 (1980).

[2] For a review of this work, see R. J. Bell, in *Methods in Computational Physics*, edited by G. Gilat (Academic, New York, 1976), Vol. 15, p. 216.

[3] A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. 64, 1564 (1976).

[4] To obtain a mode of high purity we typically quenched the system periodically approximately fifty times and then let the system run unperturbed to detect the presence of low-frequency modes and modes nearly degenerate in frequency with the desired mode. Twenty additional quenches, with longer intervals between them, were usually sufficient to purify the mode.

[5] M. H. Cohen, J. Singh, and F. Yonezawa, Solid State Commun. 36, 923 (1980).

[6] In fact what is shown in Fig. 3 is the "one-phonon part" of $S(k, \omega)$ divided by k^2.

[7] D. Weaire and V. Srivastava, J. Phys. C 10, 4309 (1977); D. C. Licciardello and D. J. Thouless, J. Phys. C 11, 925 (1978).

Ultrafast Configurational Relaxation of Optically Excited Color Centers

Jay M. Wiesenfeld and Linn F. Mollenauer
Bell Laboratories, Holmdel, New Jersey 07733

and

Erich P. Ippen
Department of Electrical Engineering and Computer Science, and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 October 1981)

The configurational relaxation time for the F_A(II) center in KCl:Li has been measured with use of picosecond laser techniques. The saddle-point configuration of the electronically excited state is stabilized by means of multiphonon emission, and has a zero-temperature lifetime of 13 psec.

PACS numbers: 61.70.Dx, 63.20.Mt, 78.45.+h

In this Letter, we report the first direct measurement of the configurational relaxation time for color centers. In particular, we have measured the rise of optical gain from the relaxed excited state (RES) of F_A(II) centers following excitation with a subpicosecond optical pulse. For the F_A(II) center in KCl:Li, we find that the configurational relaxation has a lifetime of 13 psec for temperatures below 10 K and shows a temperature dependence characteristic of a multiphonon process.

The F_A center is an F center in which one of the host cations adjacent to the vacancy is replaced by a dopant cation.[1] Type-II F_A centers are distinguished from F centers and type-I F_A centers

© 1981 The American Physical Society

by their behavior after electronic excitation: The RES of the F_A(II) center has a saddle-point configuration, in contrast to the normal, expanded vacancy configuration of F and F_A(I) centers.[1,2] The special geometry of the RES of the F_A(II) center is responsible for its utility as a tunable laser medium in the 2.5–3.3 μm range,[3,4] with use of Li-doped KCl and RbCl. To form the saddle-point configuration of the RES, a Cl^- ion adjacent to the F_A center vacancy moves to an interstitial site between a host cation and the Li^+ dopant.[1,2] As a result of the strong electron-phonon coupling in F and F_A centers,[5] many phonons in the modes coupled to the electronic transition are created in the optical (Franck-Condon) excitation process. In order for the atoms around the vacancy to stabilize in the saddle-point configuration, the vibrational energy in the optically prepared phonon modes must be damped into the dissipative continuum formed by the other phonon modes of the lattice. Thus, the configurational relaxation time corresponds to a phonon damping time. The process is analogous to that of intramolecular vibrational relaxation (IVR) in large molecules[6,7] in which molecular vibrational modes, corresponding to phonons, form a dissipative continuum.

Apart from radiative decay time measurements, there have been few dynamical studies of F-type centers.[8] In recent theoretical work, rates and yields have been calculated for nonradiative luminescence quenching in F centers by electronic curve crossing.[9,10] The configurational relaxation considered here is a first, competing process in these theoretical models.

The experimental arrangement is shown in Fig. 1. After the sample has been excited by a subpicosecond pulse at 0.61 μm, the gain is probed with a 2.6-μm cw F-center laser by using a tunable probe gating technique.[11] Pulses from the mode-locked dye laser are split into two beams (3:1 ratio). The stronger beam, the pump, is made collinear with the beam from the F-center probe laser, and both are focused to the same 40-μm-diam spot in the KCl:Li crystal. The intensity gain of the probe beam is sampled by collinear upconversion gating to 0.496 μm with the time-delayed subpicosecond pulse in an appropriately phase-matched $LiIO_3$ crystal. The time profile of the gain is obtained by varying the time delay between pump and gating pulses. The time delay is controlled by a stepping motor which indexes a multichannel analyzer, and the signal, detected with phase-sensitive electronics, is accumulated by repetitive scanning.

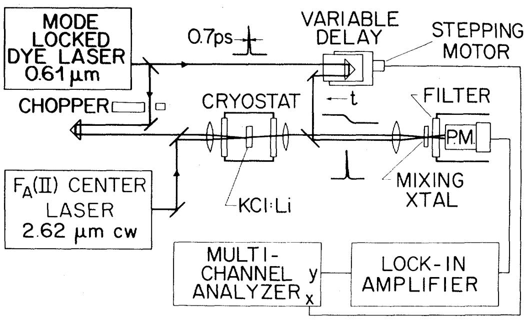

FIG. 1. Experimental schematic. The sample is pumped by a 0.7-psec pulse at 0.612 μm and probed with a cw 2.6-μm laser. The gain rise time is resolved by upconversion gating in a $LiIO_3$ mixing crystal with a time-delayed 0.7-psec pulse.

Pulses of 0.7 psec duration and 2 nJ energy are extracted from a cavity-dumped, passively mode-locked cw dye laser,[12] operating at 0.612 μm, at a rate of 250 kHz. At this rate, the sample has sufficient time to recover completely between pulses. The cw F_A(II)-center probe laser,[3,4] using a KCl:Li medium, produced 30 mW in a bandwidth less than 0.01 μm when pumped by 1.7 W at 0.647 μm.

F_A(II) centers in Li-doped KCl were created at a concentration of 2×10^{17} cm^{-3} by additive coloration.[13] The crystal was cut normal to the (1,1,1) axis, so that the parallel-polarized pump and probe beams always sampled a random distribution of centers, and no orientational bleaching effects[1] were present. The crystal was polished to a thickness of 2.1 mm and had an optical density of 0.90 at 0.612 μm at 77 K. The sample was held in a variable temperature, continuous flow liquid-He cryostat. The temperature stability was between 0.2 and 0.5 K for each period of data accumulation.

Representative time-resolved data are shown in Fig. 2. The increase in probe intensity represents only a (1–2)% gain, so that the temporal profile of the population of the relaxed excited state follows the profile of the gain. Time-resolved traces taken with a longer time base show that the gain remains constant for at least 300 psec, as expected, since the excited-state lifetime is ~100 nsec for these centers.[4] Also shown in Fig. 2 is the instantaneous system response, which is the integral of the measured pulse autocorrelation function.[14] The time origin is established to an accuracy of 0.3 psec by fitting data taken at temperatures above 30 K with the

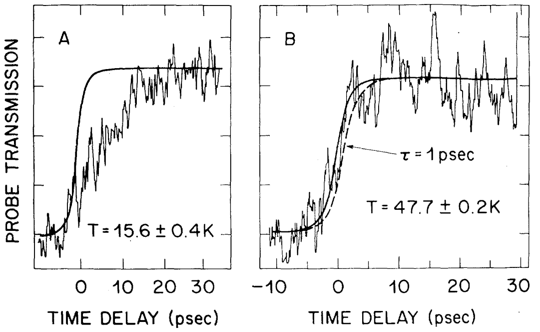

FIG. 2. Time-resolved data. The rise of gain at 2.62 μm is shown for two temperatures: (a) 15.6 ± 0.4 K, and (b) 47.7 ± 0.2 K. The solid line is the instantaneous response of the system. The dashed line in (b) is the instantaneous response convolved with a 1.0-psec rise time. Rise times are 10 ± 1 psec for (a) and < 0.5 psec for (b).

autocorrelation integral, as shown in Fig. 2(b).

Time-resolved data are fitted by an exponential rise of the form $1-e^{-t/\tau}$. Lifetimes for the rise of gain are presented as a function of temperature in Fig. 3. Traces taken at 31.6, 44.0, 47.7 [Fig. 2(b)], and 60 K all exhibit rise times less than 0.5 psec. All data shown in Fig. 3 were taken at a probe wavelength of 2.62 μm. One trace taken at 2.68 μm showed a 12.5 ± 3 psec rise time at 13.5 K, consistent with the data of Fig. 3.

The energy of the F_A(II) saddle-point configuration in KCl:Li is estimated to be 11 000 cm^{-1} above the ground state[1] and hence is 5000 cm^{-1} below the level initially populated by optical excitation at 0.612 μm. As a result of the large geometrical change between the initially excited state and the RES, there is a large Stokes shift between absorption and emission (0.6 to 2.6 μm), and the emission spectra of these states will be distinct. Thus, the appearance of emission as gain at ~ 2.6 μm is a measure of the appearance of the RES. That this state has been reached is also suggested by the constancy of the gain for periods of at least 300 psec.

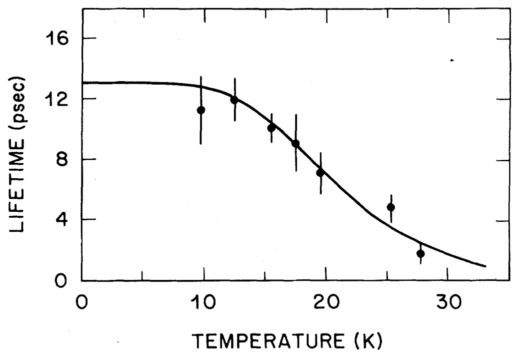

FIG. 3. Temperature dependence of relaxation times. All data shown were taken at a probe wavelength of 2.62 μm. The solid curve is a fit by Eq. (1) with the parameters $\tau(0)=13$ psec, $E_p=47$ cm^{-1}, $p=18$, and $A=0$.

The 5000 cm^{-1} of energy deposited into the phonon modes coupled to the electronic transition will ultimately be transferred to the bulk phonon modes of the lattice in a multiphonon emission process. As a result of the large density of bulk phonon modes, the configurational relaxation process corresponds to the statistical limit of radiationless transition theory.[5,6] The temperature dependence of the lifetime of a multiphonon process is often its signature, and in the limit of weak coupling is given by[15,16]

$$\tau(T)=\tau(0)e^{-A\langle n\rangle}[1+\langle n\rangle]^{-p}. \qquad (1)$$

The zero-temperature lifetime, $\tau(0)$, contains factors due to coupling matrix elements and densities of states, and resonance effects of these. Equation (1) assumes that only a single phonon mode of energy E_p is involved in the relaxation process; p phonons are created and $\langle n\rangle$ is the thermal occupation number of the mode. A is a coupling strength factor and is (much) less than 2 for weak coupling.

The temperature dependence shown in Fig. 3 can be fitted by Eq. (1) with the following ranges of parameters: $\tau(0)=12-14$ psec, $E_p=38-50$ cm^{-1}, and $p+A=12-20$. The ranges of these values are not independent. The best fit, shown in Fig. 3, is $\tau(0)=13$ psec, $E_p=47$ cm^{-1}, and $p=18$ (under the assumption $A=0$).

It is tempting to identify the mode responsible for the temperature dependence as a resonant mode involving Li$^+$ defect motion in the KCl lattice. Such a mode has been observed at 42 cm^{-1} for KCl:Li.[17] Clearly, motion of the Cl$^-$ anion from a lattice site to the saddle-point position will put a force on the Li$^+$ ion. However, this 42-cm^{-1} mode was observed in the ground state of a system without F_A centers, and its frequency will no doubt be altered in the F_A(II) excited state.

Equation (1) is an oversimplification in that it ascribes the temperature dependence to phonon modes of one frequency. Other modes must be involved in the relaxation process, since only about 900 cm^{-1} is deposited into the ~ 47 cm^{-1} mode. Bulk and localized phonon modes with energy up to 268 cm^{-1} exist for the F_A(II)-center ground state in KCl:Li.[18] The temperature dependence will be dominated by the phonon mode of lowest frequency. It is not apparent why 900 cm^{-1} is deposited into the ~47 cm^{-1} mode, since this amount greatly exceeds the energy of the highest-frequency phonon mode, and, in general, multiphonon processes occur in such a way as to create as few phonons as possible.[15] The division of energy into particular phonon modes reflects the details of coupling resonances between the optically prepared and the energy accepting phonons.[9] Relaxation may be a cascade process in the phonon mode(s) prepared by optical excitation.

It is interesting to compare the configurational relaxation process measured here to ultrafast IVR in large molecules for which there have been some direct, time-resolved measurements. For dye molecules (~120 vibrational modes), relaxation occurs in several picoseconds or less.[11,19,20] Mode-sensitive relaxation times in the range of <1 to 60 psec have been observed for IVR of pentacene substituted into crystalline naphthalene[21] or benzoic acid[22] at 1.5 K. The variety of relaxation times reflects the details of couplings and densities of states responsible for the relaxation process, as with F_A(II)-center configurational relaxation.

For ultrashort pulse generation by synchronous mode locking, the rise time for gain can affect the minimum obtainable pulse width.[23] Extrapolating the present data to 77 K, the usual operating temperature of F_A(II)-center lasers, suggests that infrared gain will appear within 0.5 psec of optical pumping. Thus, contrary to a previous speculation,[24] there are no bottlenecks in the optical pumping cycle of the F_A(II) center in KCl:Li deleterious to synchronous mode locking and pulses of picosecond duration in the 2–3 μm region should be attainable.

In summary, we have established the time scale for configurational relaxation in the electronically excited state of the F_A(II) center in KCl:Li. The relaxation is a multiphonon emission process with a lifetime that decreases from 13 ±1 psec for $T<10$ K to less than 0.5 psec for temperatures above 30 K.

We thank D. J. Eilenberger and A. M. DelGaudio for technical assistance, and J. G. Bergman, T. J. Bridges, and D. H. Olson for the loan of cryogenic equipment. We are grateful to M. G. Sceats and L. Isganitis for informative discussions.

---

[1] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[2] A. Y. S. Kung and J. M. Vail, Phys. Status Solidi (b) 79, 663 (1977).

[3] L. F. Mollenauer and D. H. Olson, J. Appl. Phys. 46, 3109 (1975).

[4] L. F. Mollenauer, in *Quantum Electronics*, edited by L. Tang, Methods of Experimental Physics, Vol. 15 B (Academic, New York, 1979), Pt. B and C.

[5] A. M. Stoneham, *Theory of Defects in Solids* (Clarendon, Oxford, 1975).

[6] K. F. Freed and A. Nitzan, J. Chem. Phys. 73, 4765 (1980).

[7] S. Mukamel and R. E. Smalley, J. Chem. Phys. 73, 4156 (1980).

[8] Very recently, a 10 ps upper limit for the nonradiative relaxation time of the F center in KCl has been reported—S. Belke, M. Schubert, and K. Vogler, Opt. Commun. 38, 369 (1981).

[9] A. M. Stoneham and R. H. Bartram, Solid-State Electron. 21, 1325 (1978).

[10] M. Kusunoki, Phys. Rev. B 20, 2512 (1979).

[11] J. M. Wiesenfeld and E. P. Ippen, Chem. Phys. Lett. 67, 213 (1979).

[12] E. P. Ippen and C. V. Shank, Appl. Phys. Lett. 27, 488 (1975).

[13] L. F. Mollenauer, Rev. Sci. Instrum. 49, 809 (1978).

[14] E. P. Ippen and C. V. Shank, in *Ultrashort Light Pulses*, edited by S. L. Shapiro, Topics in Applied Physics, Vol. 18 (Springer-Verlag, Berlin, 1977).

[15] J. Jortner, Mol. Phys. 32, 379 (1976).

[16] F. K. Fong, S. L. Naberhuis, and M. M. Miller, J. Chem. Phys. 56, 4020 (1972).

[17] R. D. Kirby, A. E. Hughes, and A. J. Sievers, Phys. Rev. B 2, 481 (1970).

[18] B. Fritz, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 496.

[19] J. P. Maier, A. Seilmeier, A. Laubereau, and W. Kaiser, Chem. Phys. Lett. 46, 527 (1977).

[20] B. Kopainsky and W. Kaiser, Chem. Phys. Lett. 66, 39 (1979).

[21] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. 74, 886 (1981).

[22] P. L. Decola, J. R. Andrews, R. M. Hochstrasser, and H. P. Tromsdorff, J. Chem. Phys. 73, 4695 (1980).

[23] C. P. Ausschnitt, R. K. Jain, and J. P. Heritage, IEEE J. Quantum Electron. 15, 912 (1979).

[24] L. Isganitis, M. G. Sceats, and K. R. German, Opt. Lett. 5, 7 (1980).