PHYSICAL REVIEW
LETTERS

VOLUME 33 26 AUGUST 1974 NUMBER 9

Polyatomic Molecular Relaxation in the Absence of Collisions*

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(Received 28 May 1974)

The fluorescence rise time for dimethyl 1, 4-bis[2(4-methyl-5-phenyl-oxazolyl)] benzene (POPOP) and perylene molecules in the vapor phase is measured with a streak camera to be less than 20 and 30 ± 10 psec, respectively. These results are direct evidence that large polyatomic molecules can rapidly relax, even in the absence of collisions.

Early theories by Zener[1] and Teller[2] predict that large polyatomic molecules relax by nonradiative processes, even in the absence of collisions. In other words, even an isolated molecule can be rapidly deactivated by these transitions. There is strong evidence for these transitions, because radiative emission from a state higher than the lowest excited state of a given multiplicity is rarely observed when large molecules are excited with a light source. Since the upper states do not emit light, they are deactivated by what is now commonly called "radiationless" electronic transitions. Indirect evidence also exists for nonradiative transitions in the absence of collision, the principal evidence being the mirror symmetry between the absorption and emission spectra for large polyatomic molecules in the vapor phase.[3] In this paper we report the first *direct* evidence of fast, picosecond, nonradiative transitions in two such large polyatomic molecules, perylene and dimethyl 1, 4-bis [2(4-methyl-5-phenyl-oxazolyl)] benzene (POPOP), in the vapor phase where the molecular collisional deactivation rate is negligible.

Recently, picosecond pulses have been used to measure vibrational and orientational relaxation times of dye molecules in the liquid state.[4-8] Nonradiative relaxation rates are measured by pumping the molecules to a higher electronic state with picosecond pulses,[9] and then observing the time dependence of the fluorescence. Because molecules relax nonradiatively to the ground vibrational states of the excited electronic state from which fluorescence takes place, the rise time of the fluorescence is a measure of the nonradiative relaxation time. For an organic molecule in a liquid the characteristic relaxation time may depend strongly on the properties of the medium. In the condensed phase a molecule collides with its environment at a rate of about 10^{12}/sec, so that in addition to decaying internally, a molecule can decay by transferring energy to its environment. The vapor state is important for establishing the fundamental nature of radiationless transitions in the isolated molecule. This is because the collision rate between molecules can be chosen to be much slower than the deactivation rate of the molecule due to radiationless transitions. Using a streak camera[10,11] technique,[12] we have measured the rise time of the fluorescence in perylene and dimethyl POPOP in the vapor phase to be $\leq 30 \pm 10$ and ≤ 20 psec, respectively. These results are significant because they definitely prove that the molecules have relaxed rapidly in the absence of collisions.

The experimental arrangement for our observations is shown in Fig. 1. A mode-locked Nd:

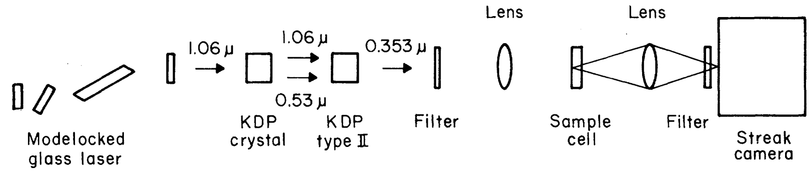

FIG. 1. A mode-locked Nd:glass laser emits picosecond pulses which are frequency tripled by two KDP crystals. A 0.353-μm, 5–8-psec pulse excites a vapor sample, and the fluorescence produced by one pulse is analyzed with a streak camera. Corning 3-73 and 3-75 filters are placed before the streak camera for the perylene and dimethyl POPOP observations, respectively.

glass laser emits a train of picosecond pulses at 1.06 μm. Satellite pulses are eliminated by use of a flowing-dye-cell arrangement on the back mirror of the laser cavity. The 1.06-μm pulses pass through the usual type-I, phase-matched potassium dihydrogen phosphate (KDP) harmonic-generator crystal producing pulses at 0.53 μm. The 1.06- and 0.53-μm pulses then pass through a second KDP crystal that is cut at 58° from the c axis for a type-II ($e+o \rightarrow e$) phase-matched sum-frequency mixing process to generate pulses at 0.353 μm. The conversion efficiency from the fundamental to the third harmonic is about 8%. These third-harmonic pulses excite the vapor samples, and fluorescence is collected and projected by a lens onto the slit of a streak camera. 1 mg of each sample was placed in 2-cm-long Pyrex cells with a volume of 13 cm^3. The cells were then evacuated and sealed off. Samples were placed inside a carefully designed copper oven, and the temperature was continuously monitored with a thermocouple output connected to a chart recorder. The streak camera used is a Los Alamos Scientific Laboratory device. The collected light is focused onto a conventional RCA-7435 grid-shuttered image-converter–type tube having an S-1 photocathode response: This tube is then followed by an image intensifier and a P-11 phosphor screen. The ramp deflection voltage was produced by an internal electronic circuit, and was triggered by an earlier pulse in the mode-locked train. The converted image of the streak was photographed on Eastman Kodak 2484 emulsion film, and the film density was calibrated with a step wedge. Densitometer traces of the resultant negatives yielded the temporal dependence of the fluorescence from which the lifetimes could be accurately deduced. The resolution time of our streak camera is about 15 psec.

Figure 2 shows a densitometer trace of a streak-camera negative of the fluorescence from dimethyl POPOP at a temperature of 295°C. The rise time of the curve in Fig. 2 was ascertained to be less than 20 psec. For perylene vapor at 300°C the rise time was measured to be ≤ 30 psec. The collision rate at these temperatures can be no more than 10^8/sec.

Because the fluorescence rise time is much shorter than the collision time, an important conclusion must be drawn, namely, that collisions are unnecessary for internal relaxation of complex molecules for times shorter than the radiative lifetimes. This rapid internal relaxation can perhaps be explained by the fact that the more complex the constitution of a molecule, the larger are the numbers of vibrational and rotational modes so that the probability of overlap and mutual interaction between these modes increases. These mutual interactions reduce the lifetime of any particular level, because any excess energy provided by the excitation wavelength can be rapidly redistributed over the large ensemble of densely packed levels. In fact, for

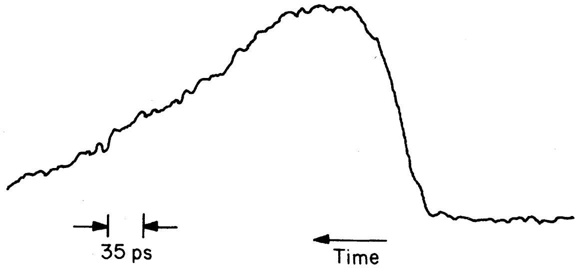

FIG. 2. A densitometer trace of a streak-camera negative shows a rapid rise time for the fluorescence from dimethyl POPOP vapor. Calibration shows that this rise time is less than 20 psec, independent of excitation intensity. The fall time is shorter for higher pumping rates because of the presence of gain in the medium. For perylene vapor the rise time is ≤ 30 ± 10 psec.

many complex molecules, no structure at all appears in the emission bands because of the mutual interactions of the levels. Spectra of dimethyl POPOP and perylene in liquids show broad featureless vibronic levels,[13] and so do the spectra of perylene in the vapor phase.[14] Because of the complexity of these two molecules, intramolecular relaxations occur independently of external perturbations. These two molecules are classified as complex according to the concepts of Neporent,[15,16] for the rate of vibrational deactivation appears to be much greater than the redistribution probabilities of the optical and nonoptical transitions to the lower electronic state.

The nonradiative redistribution of energy in molecules has attracted widespread theoretical attention recently.[17] One attractive model for molecular decay has been proposed independently by Lin and Bersohn[18] and by Englman and Jortner.[19] They have considered the problem of radiationless transitions in polyatomic molecules from the point of view of multiphonon processes, much the same as excitations decay in solids.[20] Thus giant molecules have some properties similar to a solid. In fact, some of the formalism of solid-state theory can be carried over to molecular-decay theory. Direct measurements of the fluorescence rise times in the vapor state should be most useful for refining theoretical concepts on the nature of the intramolecular decay.[21]

We thank Howard Sutphin for his aid in using the streak camera, and Dr. D. Giovanielli and Dr. G. McCall, all of Los Alamos Scientific Laboratory, for kindly lending us a streak camera.

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*Work supported by the U. S. Atomic Energy Commission.

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