Radiationless relaxation in "large" molecules: Experimental evidence for preparation of true molecular eigenstates and Born-Oppenheimer states by a coherent light source

(radiationless transitions/optical coherence/resonance decay of excited states/laser spectroscopy)

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ABSTRACT Photon absorption and emission by molecules that undergo radiationless transitions are examined using the single modes of lasers having well-defined coherence properties. Contrary to the usual beliefs, where it is assumed that the molecule is prepared in a Born-Oppenheimer singlet state and then "crosses-over" to other states (vibrationally "hot" singlets and/or triplets), it is shown *experimentally* that the true eigenstates of the molecule can be prepared, even in "large" molecules, if the laser correlation time is relatively long and the molecular relaxation is made slow. On the other hand, lasers with short (psec) correlation time have yielded *effectively* the singlet Born-Oppenheimer state, which has a much shorter lifetime than the true eigenstates. Effects of magnetic fields and temperature are also reported. The former changes the amount of mixing amongst the Born-Oppenheimer states. The latter, on the other hand, swings the molecule from being "small" (i.e., sparse vibronic structure with long lifetimes) to being "large" (i.e., dense statistical distribution of levels) since the relaxation between levels is very effective at high temperatures. Finally, the results of this work show that the words *fluorescence* and *phosphorescence* in their strict meaning are misleading if the true eigenstates, which may contain both singlet and triplet character, are prepared.

Radiationless transitions (1, 2) are extremely important processes for the description of light absorption and emission in molecules and in treating the photochemistry in excited systems. Evidence for the existence of these processes in large molecules[†] is found from the measurements of quantum yield of fluorescence, which turn out to be less than one and effectively the same in the gas phase and in solution. These observations indicate that the processes do exist in the so-called "isolated molecule" and that they must occur by an intramolecular mechanism. Parmenter and coworkers (3–5) have studied benzene at very low pressures and found the quantum yield to be less than one. This point raised the concern that the results cannot be explained by the simple laws of quantum mechanics.

In large molecules one usually finds that the lifetime is *shorter* than the radiative lifetime (obtained from oscillator strength measurements), and the quantum yield is *less* than one. On the other hand, Douglas' work (6, 7) on small molecules has shown that the measured lifetime is *longer* than the radiative one while the quantum yield is close to unity. This paradox was resolved by incorporating different coupling mechanisms among the Born-Oppenheimer (BO) states.

The use of BO states raised another question that pertains to the calculation of nonradiative decay rates using different versions of BO approximations. However, the qualitative picture is basically the same. The molecule has a "primary" state (e.g., singlet electronic state) ϕ_p and a ground state ϕ_0. Isoenergetic with ϕ_p there exist many other levels from the lowest triplet manifold or the vibrationally hot levels of ϕ_0 (see Fig. 1). The coupling matrix element between ϕ_p and the other levels, and the density of states in the neighborhood of $|p\rangle$ [i.e., $\rho_l(E_p)$ and $\rho_t(E_p)$] determine the routes of the nonradiative decay. In many ways this scheme resembles Fano's description (8) for the autoionization of helium. However, in molecules, irreversible electronic relaxation deactivates excited levels without the ionization of the molecule or the rearrangement or the breaking of chemical bonds.

Robinson's group (2) has shown that irreversible (1) electronic relaxation of molecules in condensed phases results from the medium that provides a heat bath. Further, they argued that in isolated large molecules the density of states is sufficiently high that they form the intramolecular sink in the molecule (statistical limit). The true molecular states considered by Bixon and Jortner (9, 10) are mixtures of ϕ_p and the quasicontinuum states, and their superposition forms the nonstationary ϕ_p state, which evolves in time according to the exact Hamiltonian.

In the above description, it is *assumed that in the statistical limit the light initially prepares* ϕ_p excitation, which may then fluoresce or "cross-over" to the quasicontinua. If the density of states is high enough, the "theoretical recurrence" (due to Poincaré) might be much longer than the time scale of the experiment (11). In isolated molecules (low pressure gases) spontaneous infrared emission (12) from the vibrationally hot $\{l\}$ and $\{t\}$ manifolds, collisions with the wall, and the time scale of the experiment will determine the irreversibility of these electronic relaxations. Further, the "crossing-over" process reflects the exact nature of the molecule-photon interaction (13) discussed recently by many investigators. The articles by Rhodes *et al.* (14–16) have addressed the question of the effect of the exciting light bandwidth on the initial state preparation. Since then different mathematical techniques have been used to answer these questions. The stationary state approach, effective Hamiltonian formalism, Green's function techniques, and the density operator method examine the various correlation and relaxation times when the light source interacts with the molecular system (1, 2). Couched in these theoretical thoughts, one would like to ask the following questions: *In the laboratory, do we really excite the BO states of large molecules? If we normally do this, then is there any other experimental means by which we can instead prepare the true eigenstates of such molecules?*

In this paper we present experimental evidence for the

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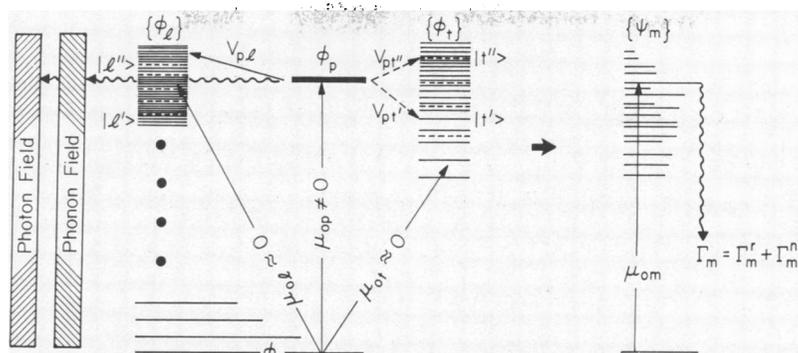
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FIG. 1. The different pathways for electronic relaxation in large molecules. *Left.* BO representation. *Right.* True eigenstates of the system. Notice the phonon field results in a spectral broadening while the photon field mediates the spontaneous decay processes. ϕ_p, ϕ_0, ϕ_l, and ϕ_t = zeroth order BO states; ψ_m = molecular eigenstate; $\Gamma_m{}^r$ = radiative rate; $\Gamma_m{}^{nr}$ = nonradiative (irreversible) electronic relaxation rate.

preparation of true eigenstates of a large molecule (pentacene). It is also shown that (*a*) BO states[‡] can be prepared if the correlation time of the laser source is sufficiently short (psec), (*b*) the coupling between the zeroth-order BO states is very sensitive to the mixing between the $|p\rangle$ state and the triplet manifold, as evident from our magnetic field experiments, and finally (*c*) the molecule can be swung from the sparse limit to the statistical limit by controlling the temperature of the bath in the presence of the exciting coherent source.

Methodology

The idea of these experiments is to excite the vibronic states of a large molecule by both broad and narrow band excitation sources, and to measure the phase coherence and the incoherent decay of these selectively prepared states after the excitation. The results must reflect the role of state preparation and the nature of the coupling amongst the zero-order BO states. Two different coherent sources were used for the excitation of the electronic origin near 16,882 cm^{-1} of pentacene in *p*-terphenyl (17, 18). For broad band excitation, a dye laser (Molectron model DL 200) pumped by a nitrogen gas laser (Molectron model UV 400) was used. For narrow band excitation, we used the technique (19) of incoherent resonance decay (IRD) developed by Zewail, Orlowski, and Dawson.

A single-mode of a tunable dye laser was used to pump a selective molecular packet (resolution $\approx 10^{-4}$ cm^{-1}) that is hidden under the inhomogeneous resonance of the mixed crystal. The laser was then switched (20) electro-optically by a voltage pulse on a nonlinear crystal (AD*P). This switching shifts the laser frequency by an amount that is adjusted to be larger than the intrinsic "homogeneous" width of the transition. The change in the emission intensity before and after the switching was monitored by a box-car integrator (PAR, model 162) while the bath was at different temperatures (1.7 K–4.2 K). Magnetic fields up to 900 G were used to probe the amount of triplet state mixing in the true eigenstate decay that is detected by the IRD method. This method is very sensitive and very selective in preparing the excited state since the laser width (which has an excellent transverse Gaussian profile) is only 6 MHz.

Preparation and decay of excited states in "large" molecules

The vibronic structure in a large molecule like pentacene with 102 optical modes belongs to the statistical limit where the density of vibrationally hot ground states in the neighborhood

[‡] By BO state we mean a zeroth order state that carries most of the oscillator strength from the ground state.

of $|p\rangle$ is very large. However, pentacene (21–25) is known to have nearby BO triplet states. Moreover, not all the modes in the $\{l\}$ continuum are *active* in the coupling with $|p\rangle$ because of the symmetry requirement and/or the Franck-Condon overlap. Effectively, one says that the molecule has an intermediate level structure (26, 27) that exhibits two coupling schemes, strong coupling with a sparse active level and weak coupling with a dense continuum. Quantum mechanics therefore tells us that the eigenstates of ϕ_p and $\{\phi_j\}$ can be written as

$$\psi_m = \mathcal{A}_{pm}\phi_p + \sum_j \mathcal{A}_{jm}\phi_j \qquad [1]$$

where the sum is over all the *j* active levels.

Monochromatic preparation of ψ_m makes the system evolve in time by the quantum mechanical stationary state characteristics and by the Weisskopf-Wigner damping term:

$$\langle \psi_m | \psi_m(t) \rangle = \langle \psi_m | e^{-i\mathcal{H}t/\hbar} | \psi_m \rangle = e^{-iE'_m t/\hbar}. \qquad [2]$$

E'_m contains the imaginary energy term that describes the decay:

$$E'_m/\hbar = E_m/\hbar - \tfrac{1}{2} i\Gamma_m{}^r - \tfrac{1}{2} i\Gamma_m{}^{nr}. \qquad [3]$$

One notes that the effect of relaxation on the true eigenstates of the system is contained in the Γ matrix whose radiative damping matrix elements [the coupling between the molecular state and the photon field (11), see Fig. 1] are

$$\Gamma_{nm}{}^{(r)} = \frac{2\pi}{\hbar} \sum_\alpha \sum_e \int d\Omega_k \langle n | \mathcal{H}_{int} | \alpha, ke \rangle$$

$$\times \langle \alpha, ke | \mathcal{H}_{int} | m \rangle \rho_{photon}(\omega) \qquad [4]$$

where $\mathcal{H}_{int}$ is the matter-field Hamiltonian and the summation is over all lower states α to which *m* and *n* may spontaneously decay, and *e* is the polarization. The nonradiative decay matrix elements, $\Gamma_m{}^{nr}$, similarly depend on the density of dissipative states and the coupling matrix elements. Assuming a diagonal Γ (i.e., no correlation amongst the decay channels), the total decay can be related to the BO states using Eq. 1:

$$\Gamma_m = |\mathcal{A}_{pm}|^2 \Gamma_p + \sum_j |\mathcal{A}_{jm}|^2 \Gamma_j. \qquad [5]$$

Eq. 5 says that if the coupling between $|p\rangle$ and $\{j\}$ (the states with essentially zero oscillator strength) is effective, *the "large" molecule obeys the laws of the "small" molecule limit.* In other words, the lifetime of the monochromatically prepared state becomes longer than $1/\Gamma_p$.
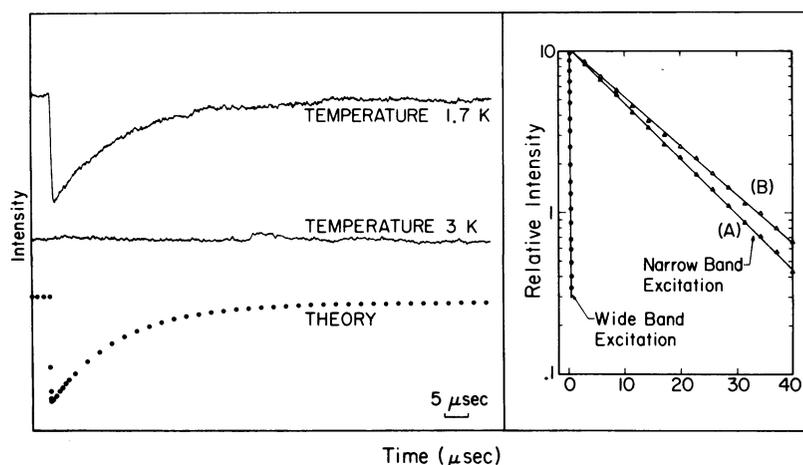
FIG. 2.   The top left spectrum is the IRD signal observed using the single mode of the dye laser that is *on* resonance with the molecular transition. The bottom left spectrum is the IRD at high temperature (above 3 K). At high temperature the dc current of the photomultiplier increased. The trace at high temperature (the liquid helium was gone) was taken at the same dc level as the low temperature one. The solid circles are the theoretical fit for the IRD pattern. The build-up that contains the laser pump term must also include the molecule-photon scattering process. The inset in the figure shows the decay of the excited electronic origin of pentacene as a function of the laser bandwidth. *A* and *B* are the decay rates following the laser narrow band excitation in zero and applied magnetic field. In these experiments the magnetic field was turned on and off 10 times and consistently the decay was found to change by ≈15%, which we ascribed as due to the triplet mixing with the $|p\rangle$ state. The standard deviation on these decay measurements is small (2%), but a larger error of 8% was found when we considered the reproducibility of the measurements on different crystals and with different laser power and frequency. Note that the field affects what will be called "fluorescence."

The above narrow excitation process is different from the so-called broad band excitation (9, 10) which implicitly assumes that the exciting pulse is a delta function in time! If the light source has an energy spread comparable to the inhomogeneous[§] width (9, 10), the excitation of a large molecule like pentacene will form a coherent or incoherent combination of ψ_m's, depending on the relative phases of the emitters (or modes) in the light source. Because the molecule is in the ground state at $t = -\infty$, semiclassically the system will evolve in time in the interaction representation as follows ($\hbar = 1$):

$$\psi'(t) = \psi'(0) + i \int_{-\infty}^{t} e^{i\mathcal{H}mt'}[\mu \cdot E_0 \delta(t')]e^{-i\mathcal{H}mt'}\psi'(t')dt'$$

[6]

where μ is the transition dipole operator and E_0 is the amplitude of the field. Using the above interaction representation picture, one therefore concludes that the δ-function excitation prepares the primary state at $t = 0$ since ϕ_p is optically allowed:

$$\psi(t = 0) = i\langle\phi_p|\mu \cdot E_0|\phi_0\rangle \sum_m |\psi_m\rangle\langle\psi_m|\phi_p\rangle + |\phi_0\rangle[7]$$

For transform limited light pulses that create the $|p\rangle$ state the time evolution will not only have a decay but also recurrences, oscillations, etc. One can solve the problem exactly by calculating the amplitude of the decay from the convoluted Green's function of the system (28–30). In the Schrödinger representation, this probability of finding the system in $|p\rangle$ following its initial creation is given by (Eqs. 1, 2, and 5):

$$\mathcal{L}_p(t) = |\langle\phi_p|e^{-i\mathcal{H}t/\hbar}|\phi_p\rangle|^2$$

$$= \left|\sum_m |\mathcal{A}_{pm}|^2 e^{-iE'mt/\hbar}\right|^2.$$

[8]

Eqs. 7 and 8 indicate that the excitation of the system creates a metastable state that carries most of the oscillator strength and decays rapidly if the source spans the set of molecular eigenstates that are now coherently excited. We should add that the optical dephasing (T_2) processes in these large molecules is very important, especially at short times. However, both optical T_1 and T_2[¶] of the system under study are known experimentally (31–33) and we need not speculate about their influence on the theoretical treatment.

Experimental results and discussion

At very low temperatures (1.7 K) pentacene in *p*-terphenyl exhibits site splittings; four distinct origins have been identified. The single mode of the dye laser excited the O_1 origin (17, 18) at 16,882 cm^{-1}. At the same time the coherent transients in the forward direction of the laser beam, the emission at right angles, and the spectrum of the single mode were monitored. Fig. 2 shows the selective emission of the O_1 origin when the laser was switched into other molecular packets (thus allowing the original packets to decay) within the inhomogeneous line. It is clear that the decay of the state following the narrow width preparation (about 10^{-4} cm^{-1}) takes much longer time than that anticipated for the allowed singlet BO state.

Our observation of 15 μsec for the decay time constant indicates that the true eigenstates, and *not* the BO state, were prepared by the laser. This means that the mixing between $|p\rangle$ and {*j*} states is relatively strong. In the language of photon correlation spectroscopy (34), one says that the excitation correlation time ($\pi/\Delta\omega$) is ≥10^{-6} sec (i.e., photon coherence length of 300 m). This time is much longer than the internal coupling correlation time, $\pi/\Delta E$, which is on the order of picoseconds. ΔE is the energy spread involved in the coupling between $|p\rangle$ and {*j*}. Knowing the decay constant and the correlation time from our experiments, and assuming a uniform coupling amongst all active levels, one, in fact, can obtain the distribution

[§] The word *homogeneous* means the intrinsic resonance of the molecular emitters. By inhomogeneous resonance we mean a statistical distribution of many homogeneous isochromates (or packets). This inhomogeneous broadening could be either due to "molecular inhomogeneity" (i.e., many unresolved molecular states) or "crystal inhomogeneity" due to differences in crystal fields.

[¶] T_1 and T_2 are the optical analogs of magnetic resonance relaxation constants. T_1 is the spontaneous decay time, while T_2 gives the degree of coherence in the excited ensemble.

of the oscillator strength over the inhomogeneous width in the neighborhood of the primary state.

The coherent coupling between molecular states and the laser field involves two different groups of molecules; one group (β) is decaying following the laser switching, and the other (α, at the new laser frequency) is building up population with well-defined phase coherence. The solution for the averaged density matrix describing these two subensembles with the inclusion of dephasing processes gives a build-up and decay for the following diagonal matrix elements (population density) which determine the emission pattern:

$$\langle \rho_{mm}^{(\alpha)}(t) + \rho_{mm}^{(\beta)}(t) \rangle = \{B(T_1,T_2,\mu \cdot E_0;t)\}_\alpha$$
$$+ \{D(T_1,T_2,\mu \cdot E_0)e^{-\Gamma_m t}\}_\beta. \quad [9]$$

The build-up function, B, reaches the saturation limit very fast since $\mu \cdot E_0$ is large. The spontaneous relaxation (T_1^{-1}) and dephasing (T_2^{-1}) rates determine the build-up characteristics, while T_1^{-1} alone determines the decay of the IRD. Since we know that the dephasing time for the molecular dipoles is very short (25 nsec) compared with $T_1(1/\Gamma_m)$, the random phase approximation can be used at *long* times. The average in Eq. 9 is over the inhomogeneity of the laser and the crystal. The theoretical calculation for the observed IRD pattern of pentacene in *p*-terphenyl at 1.7 K is shown in Fig. 2. Fig. 2 also depicts the IRD at low and high temperatures. The disappearance of the signal above 3 K indicates that the communication rate in the vibronic manifold is becoming fast compared to our switching time. This means that as far as the time scale of the experiment, the system recovers the statistical limit one expects for large molecules at high gas pressures or high solid temperatures. This is consistent with the loss of coherence that we observed in these systems above 3 K due to the increase of phonon population. The details of these studies on the temperature dependence will be described elsewhere (A. H. Zewail, K. E. Jones, and T. E. Orlowski, unpublished data).

As pointed out before, the coupling between $|p\rangle$ and the active levels of $\{t\}$ and $\{l\}$ can be distinguished because of the finite spin angular momentum of $|t\rangle$ states. When we applied a magnetic field B on unoriented crystals, about 15% change in the decay at low temperatures was observed (Fig. 2). This means that the $\mathcal{A}_{jm}$ values of Eq. 1 are B-dependent and, thus, there must be an effective coupling between the zero-order BO $|p\rangle$ state and its neighboring $|t\rangle$ levels. The question is, of course, does the mixing enhance or decrease when B is turned on. Because the lifetime gets longer, it would seem that B is bringing in triplets, consistent with earlier findings (23, 25) that hot singlet states of ϕ_0 are involved. However, further detailed studies on single crystals will clarify this point.

The above observations show that in the narrow band excitation we have prepared the true eigenstates of the molecule. The question is, *how can we prepare the BO* $|p\rangle$ *state?* To do this we used the output of the pulsed dye laser because its correlation time is on the order of picoseconds. Therefore, by Eqs. 6–8 one predicts that the laser excitation should produce a nonstationary state that is decaying *effectively* by the radiative and nonradiative rate constants. Fig. 2 shows our experimental results, which compare the narrow band excitation with the broad band excitation of pentacene in *p*-terphenyl at low temperature. The results show, first, a dramatic (about two orders of magnitude) shortening of the lifetime when a large number of eigenstates is exposed to the excitation source. This gives clear evidence for the effect of molecular state preparation on the dynamics (radiative and nonradiative) of excited state photophysical processes. Second, the nonradiative decay must not be the effective channel for the loss of excited state popu-

lation; the decay is from molecules that are vibrationally "hot" but thermally "cool". In fact, Γ^{nr} must be less than 10^5 sec^{-1}. Raising the temperature enhances intermolecular coupling with the bath that opens the nonradiative routes. Finally, contrary to photon echo experiments which measure a T_2 that could be the same for the BO state and the true eigenstates, the IRD technique shows the distinct differences in T_1 induced by the nonradiative decay and the radiative mechanism of Eq. 5. For pentacene in terphenyl it is therefore concluded that the optical dephasing is much faster than the spontaneous lifetimes of ψ_ms, indicating that elastic scattering of phonons is more operative than the inelastic processes at these temperatures. These observations alarm us about the words *fluorescence* and *phosphorescence* which, in their strict meaning, do not give an accurate description, especially if the true eigenstates of the system contain a large fraction of triplets. These findings on the nature of intramolecular (35) and intermolecular (36) radiationless transitions in large molecules are of great interest to theorists and experimentalists who work in the fields of photophysics and photochemistry.

Note Added in Proof. Recently, with a resolution of 10^{-4} cm^{-1} we have observed the optical free induction decay in molecular beams and the photon echo on the *spontaneous emission* of gases near zero pressure. These observations (*Chem. Phys. Lett.*, in press) which give optical T_1 and T_2 in gases and beams will now allow us to separate the mechanisms for the spontaneous and dephasing processes at zero pressure (intramolecular) and in condensed phases.

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