changes in the iron–porphyrin distances upon oxygenation. Similar iron–porphyrin bond lengths (within 0.02 Å) were found in low-affinity deoxy-HbA and high-affinity deoxy-Hb Kempsey, indicating that the restraint in the T form is introduced upon oxygenation. This is further supported by resonance Raman results[37b] of Fe–N(axial) bond length changes for T and R Hb Kempsey which account for no more than 0.2 kcal mol^{-1} for heme.

A weakened iron–proximal histidine interaction results in weaker iron–nitrogen and metal–dioxygen bonds in the T form than they would be in the absence of the restraint. In this manner, coordination of dioxygen stores potential energy in the system that could be released if the iron–nitrogen restraint were removed by a protein conformational change. Not enough energy for the protein change is generated upon binding the first dioxygen. Multiples of this potential energy are stored on binding the second and third dioxygens. Note that potential energy is stored from a stronger metal–base interaction as well as a stronger dioxygen interaction for each bound oxygen. Upon coordination of the third dioxygen more than enough potential energy is available in the system from the increased iron–nitrogen and iron–O_2 bond strengths that would exist in the R form to effect the endothermic T to R protein transformation. Addition of the fourth dioxygen is expected to be the most exothermic of all the O_2 binding steps (see Figure 4) because the O_2 coordinates to an iron in the R form.

In this model, all of the structural changes in the iron relative to the porphyrin are similar in Hb to those observed in systems not exhibiting cooperativity; hence, the proximal imidazole interaction is the key to cooperativity. An energy balance to account for the 3.5 kcal mol^{-1} difference in the O_2 binding affinity of high- and low-affinity forms is difficult. If the T to R protein transformation is endothermic, this energy plus the 3.5 kcal mol^{-1} is distributed over the 3 metal–oxygen, 3 iron–proximal imidazole, and 12 iron–porphyrin nitro-

gen interactions in the O_2 adduct.

The decreased extent of cooperativity found in CoHb relative to Hb does not provide any insight regarding cooperativity.[38a-c] In view of the preceding discussion, we see that the problem is very complex. The potential energy gained and stored upon oxygen complexation would depend on the relative cobalt–base or iron–base bond energies as well as on the sensitivity of the dioxygen–iron or –cobalt bond strengths to coordinated axial base strength.

Clearly, two features of the cooperativity model have fallen into place. First, the affinity of the Hb is dependent on the Fe–histidyl bond strength. We favor the bending of the Fe–N(axial) bond in the oxygenated T form arising from restraint of the histidine residue by the globin. Nonbonded contacts between the proximal histine and the heme have been suggested[39a-c] as providing a mechanism for cooperativity. The excellent fit of the cobalt porphyrin oxygen binding enthalpies to our E and C equation suggests that steric effects are not operative in this system. Furthermore, it is difficult to see how the protein conformation can cause the heme unit to be domed toward the proximal histidine in one state and not the other. The configurational changes about the iron are expected to be the same upon oxygenation of the T and R forms of the protein unless restraint in the histidine–iron interaction is operative.

The second salient feature of cooperativity is that most of the potential-energy difference between the two quaternary deoxy states arises from hydrogen-bonding interactions in the protein and not from the heme unit. The subtle geometrical changes about the iron that occur upon oxygenation are insignificant relative to the changes in the globin.

(38) (a) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.*, **1970**, *92*, 55. (b) Schiedt, W. R.; Dwyer, P. N.; Madera, P. *Ibid.* **1974**, *96*, 4815. (c) Little, R. G.; Ibers, J. A. *Ibid.* **1974**, *96*, 4452.

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Optical Molecular Dephasing: Principles of and Probings by Coherent Laser Spectroscopy

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Coherent laser spectroscopy of large molecules is a new and challenging area of study. The strength of this type of optical spectroscopy is that it can probe important dynamical molecular processes that are not

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amenable to conventional methods such as absorption and emission spectroscopy. One such dynamical process is optical dephasing.

When a laser interacts with an ensemble of molecules, under certain conditions, one can create a coherent linear combination of ground and excited molecular wave functions. This coherent state, or what is sometimes called a pure state, possesses a definite phase relationship between the wave function of the ground

and excited states. Due to interactions of the optically excited molecules with themselves or with the environment, the coherent state can become incoherent. In other words, the well-defined superposition of states created by the laser becomes random or statistical in nature. Randomization of phase coherence in time is termed dephasing, and the processes behind the phenomenon are the dephasing mechanisms.

Optical dephasing processes are currently of considerable interest, primarily because of the many intra- and intermolecular interactions that they manifest. For example, molecules optically excited to a vibrational state in a liquid can dephase by vibrational energy relaxation and by elastic collisions which leave the molecule in the same vibrational state. One would like to predict which of these two relaxation processes, energy or pure phase, is dominant, and whether or not they are determined by molecular structure parameters. Similar questions can be raised about molecules under isolated conditions. Consequently, dephasing plays a fundamental role in the dynamics of photophysical and chemical events including laser-induced selective chemistry and molecular multiphoton dissociation.

One might ask: Why use coherent laser spectroscopy, and what is wrong with using "conventional" spectroscopic methods to measure dephasing? For the conventional steady-state optical experiment, there are two basic observables: the resonance line position and line shape. Line positions indicate transition energies: electronic, vibrational, or rotational. Line widths are a composite of a number of dynamical effects. In general, the width, $\Delta\nu$, of a single two-level transition is related to a time Δt by the uncertainty principle. Several processes, including pure dephasing, contribute to the apparent Δt. The lifetime of the excited state, measured by conventional fluorescence decay experiment, will only give the lifetime contribution to Δt, or the lifetime broadening to $\Delta\nu$. On the other hand, experiments which measure the overall $\Delta\nu$ cannot separate the energy and phase relaxation times. It is in this separation of energy and phase relaxations of spectroscopic transitions where coherent laser spectroscopy can contribute!

In this Account I will discuss some of the work in our laboratory and focus on (a) the principles of coherent laser spectroscopy and (b) how it is used to examine chemical and physical processes relevant to molecular systems.

Quantum Origin of Optical Dephasing

Two questions are relevant here. First, what is measured in a coherent optical experiment? Second, is the measured optical coherence due to some quantum effects in the molecule? Measurements of optical dephasing require the following: first, the coherent laser preparation of a set of molecules in a given vibronic or rovibronic state; second, the probing of the prepared coherent state as time goes on and the molecules dephase by, e.g., vibrational-to-vibrational energy flow. For the coherent preparation, the laser must satisfy certain requirements and for the probing one must gauge the time dependence of the nonlinear coupling between the molecules and the radiation field, the laser. Throughout this Account I shall consider only the semiclassical approach—the molecule is treated quantum mechanically and the laser field classically. Doing
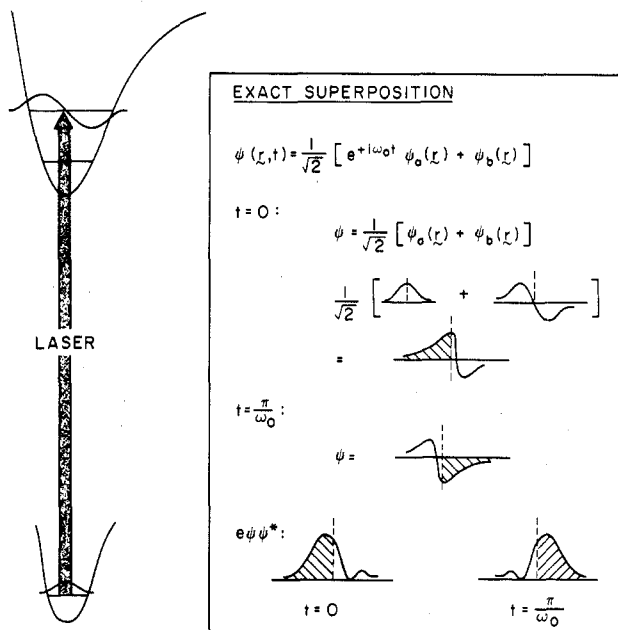

Figure 1. A schematic (rough) description of optical coherence in molecules.

this allows one to shine some light on the above two questions but will not provide a rigorous description of the origin of the incoherent spontaneous emission since the radiation field is not quantized in the semiclassical picture.

Semiclassically, we describe the phenomenon as follows: the laser field E interacts with an ensemble of molecules to produce a time-dependent polarization, $P(t)$, which in turn changes as the molecules dephase. So, our task now is to find how the polarization is related to dephasing and what dephasing means on the molecular level. It is instructive to examine critically the origin of dephasing in molecules with only two levels.

Consider two vibronic states: a ground state, $\psi_a(\mathbf{r})$, and an excited state, $\psi_b(\mathbf{r})$. The laser field is simply a wave (propagation direction, z) of the form

$$E(z,t) = \epsilon \cos(\omega t - kz) = \frac{1}{2}[\epsilon e^{i(\omega t - kz)} + \epsilon e^{-i(\omega t - kz)}] \quad (1)$$

where ϵ is the amplitude and ω is the frequency of the radiation. The state of the molecule (driven by the laser) at time t may be represented as

$$\psi(\mathbf{r},t) = a(t)e^{-i\omega_a t}\psi_a(\mathbf{r}) + b(t)e^{-i\omega_b t}\psi_b(\mathbf{r}) \quad (2)$$

We now can calculate the time-dependent molecular polarization:

$$\begin{aligned} P_m(t) &= \langle\psi(\mathbf{r},t)|\hat{\mu}|\psi(\mathbf{r},t)\rangle \\ &= ab^*\mu_{ba}e^{-i(\omega_a-\omega_b)t} + a^*b\mu_{ab}e^{-i(\omega_b-\omega_a)t} \end{aligned}$$

$$(3)$$

where $\hat{\mu}$ is the dipole-moment operator and μ_{ba} and μ_{ab} are the transition moment matrix elements. Taking these matrix elements to be equal ($\equiv\mu$) and setting $\omega_b - \omega_a = \omega_0$, the transition frequency, we obtain

$$P_m(t) = \mu[ab^*e^{+i\omega_0 t} + a^*be^{-i\omega_0 t}] \quad (4)$$

Hence, the polarization, which is related to the radiation power, is zero if there is *no* coherent superposition or, in other words, if the molecule is certain to be in the state a or b. As shown in Figure 1, as a result of the superposition of states the charge in a volume element

dv, $e\psi\psi^*$dv, oscillates coherently between two distributions and the system is nonstationary. From eq 4 the total polarization for N molecules in the sample (assuming equal contribution and ignoring propagation effects) is therefore

$$P(t) \equiv \frac{1}{2}[\bar{P}e^{i\omega_0 t} + \bar{P}^*e^{-i\omega_0 t}] = N\mu[\rho_{ab} + \rho_{ba}] \quad (5)$$

where $P(t) \equiv NP_m(t)$ and $\bar{P}$ is its complex amplitude, i.e., $\bar{P} = \bar{P}_{real} + i\bar{P}_{imag}$. We chose the notation ρ_{ab} and ρ_{ba} for the cross terms $ab^*e^{+i\omega_0 t}$ and $a^*be^{-i\omega_0 t}$ because they are indeed the off-diagonal elements of the ensemble density matrix ρ.

So far all that we have shown is that to create a polarization or optical coherence we need a nonvanishing interference term or equivalently the off-diagonal elements of ρ must be nonzero in the zero-order basis set. Quantum mechanically, one can calculate these coherence terms and, for the most experimental descriptions, one can perform a rotating coordinate frame analysis for the components of P. Although I will give an illustrative example for calculating P later, the reader is encouraged to see the more detailed calculation given in the excellent text by Sargent, Scully, and Lamb.[2]

Now that we have obtained the polarization, the resultant coherent field in the sample can be found using the following self-consistent prescription:

laser field + molecules $\longrightarrow$

polarization, $P \longrightarrow$ sample field (6)
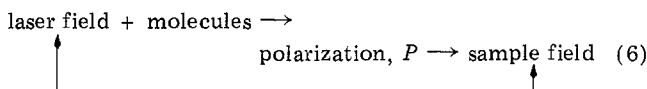
Basically, P can be calculated by using eq 5, and Maxwell's equations can be used with $\bar{P}$ being the source term to calculate the resultant sample field amplitude $\bar{\epsilon}$. It is through $\bar{P}$ (or $\bar{\epsilon}$) that we can monitor the nonlinear optical behavior of the sample and hence the changes in the rate of optical dephasing. Before calculating the polarization or the sample field it is useful to know the connection between optical dephasing and optical spectroscopy and the different types of dephasing.

Homogeneous and Inhomogeneous Dephasings: Optical T_1 and T_2

From eq 2 we see that the probability of finding the system in the excited (ground) state is simply $|b|^2$ ($|a|^2$). These probabilities decay by time constants, say T_{1b} and T_{1a}, respectively. Such phenomenological decay is the result of the Wigner–Weisskopf approximation, i.e., an exponential decay of the amplitudes a and b; a or $b \propto e^{-t/2T_1}$. Also, the cross terms of eq 2 will decay possibly by a different rate from the diagonal terms. Hence, the ensemble density matrix can now be written as

$$\begin{array}{cc} |a\rangle \equiv \psi_a(r) & |b\rangle \equiv \psi_b(r) \\ \langle a| & \begin{bmatrix} |a_0|^2 e^{-t/T_{1a}} & (a_0 b_0^* e^{+i\omega_0 t})e^{-t/T_2} \\ cc & |b_0|^2 e^{-t/T_{1b}} \end{bmatrix} \end{array} \quad (7)$$

where

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2}\left(\frac{1}{T_{1a}} + \frac{1}{T_{1b}}\right) \quad (8)$$

The T_1 term in eq 8 comes from the diagonal elements

(2) M. Sargent III, M. Scully, and W. Lamb, Jr., "Laser Physics", Addison-Wesley, Reading, MA, 1974.

and represents an average rate for the loss of population in the ab levels. Physically, the T_2' term represents the additional decay caused by phase changes in the cross terms. In other words, the random and rapid variation in $\omega_0(t)$ causes the off-diagonal elements to decay faster than the diagonal ones. One can show that the linewidth of the transition a–b is $1/(\pi T_2)$ if the band profile is Lorentzian. The total dephasing rate is therefore $1/T_2$: It contains $T_2'^{-1}$ the rate for phase coherence loss (pure dephasing), and T_1^{-1}, the rate for irreversible loss of population in the two levels. The phenomenology described here is the optical analogue of magnetic resonance T_1 and T_2 of Bloch's equations,[3] but as we shall see later, the physics is different.

If we monitor emission, say, from b, it is clear now that all we can measure is T_{1b}. Furthermore, if the ensemble is homogeneous (i.e., consists of only those molecules that follow the uncertainty relationship $\Delta\nu T_2 = \pi^{-1}$), then an absorption experiment will give T_2 and an emission experiment will give T_1 and we have T_2' at hand. Unfortunately, there are two problems. First, the optical transitions are inhomogeneously broadened (IB). This implies that the homogeneous ensemble is a subensemble of a grand ensemble as, e.g., in the case of Doppler broadening in gases. Because of IB, the homogeneous resonance is hidden under the usually broader IB transition. Similar to homogeneous widths, the width of IB transition can be related to a dephasing time, T_2^*, by using the uncertainty relationship.

The second problem concerns the measurement of T_2. If the homogeneous broadening (HB) is very small, it is difficult to measure HB through absorption methods by using state-of-the-art lasers. By time-resolved experiments, however, the narrower the resonance, the longer the decay time, and it is relatively easy to measure T_2. It is this ability to separate T_2 (T_1 and T_2') and T_2^* with ease that makes coherent laser spectroscopy a useful technique for unravelling dynamical optical processes in molecules. For example, most large molecules in low temperature solids show IB of $\sim$2 cm^{-1}, which implies that $T_2^* \sim 5$ ps. If T_2^* were interpreted simply in terms of intrinsic HB, it would be said that all these molecules in solids dephase on the picosecond time scale. As we shall see later, this is not true and, in fact, the HB is orders of magnitude smaller than the IB, especially at low temperatures.

Experimental Probing of Dephasing

For the sake of clarity, let us now calculate the polarization and the field of a typical ensemble of molecules. Using the time-dependent Schrödinger equation one can quite easily obtain a and b of eq 2. On resonance, i.e., when $\omega = \omega_0$, and in the absence of relaxation

$$a(t) = \cos\left[\frac{1}{2}\left(\frac{\mu \cdot \epsilon}{\hbar}\right)t\right] \equiv \cos\frac{\omega_R t}{2} \quad (9)$$

$$b(t) = -i\sin\left[\frac{1}{2}\left(\frac{\mu \cdot \epsilon}{\hbar}\right)t\right] \equiv -i\sin\frac{\omega_R t}{2} \quad (10)$$

where ω_R is the Rabi frequency ($\mu \cdot \epsilon/\hbar$). Note that the total Hamiltonian now contains the molecule–radiation interaction Hamiltonian ($\hat{\mu} \cdot E$). From eq 9, 10, and 5,

(3) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961.

polarization is maximum when $\omega_R t = \pi/2$ and that is why $\pi/2$ optical pulses are very desirable. At time $t = \pi/(2\omega_R)$, P_m becomes simple: $P_m = -\mu \sin \omega_0 t$. This polarization is created out-of-phase with the applied field, $\epsilon \cos \omega t$, as it should. We now suppose that we are starting with N_b molecules per unit volume in state b and N_a in state a. If the exciting field is turned off at $t = \pi/(2\omega_R)$, then the net macroscopic polarization, or radiating dipole moment per unit volume, is

$$P = -(N_a - N_b)\mu \sin \omega_0 t \qquad (11)$$

Hence the net radiated power per unit volume ($\langle E_c(t)dP/dt \rangle$, time averaged) is

$$\text{net power} = \frac{N_b - N_a}{2}\omega_0(\mu\bar{\epsilon}) \qquad (12)$$

where $\bar{\epsilon}$ is the field amplitude created by the radiating molecules since now the external field is off.

For the coherent coupling to take place between the molecules and the applied field, the inequality $\omega_R > 1/T_2$ must hold. Near the coherent limit we can therefore estimate the laser field amplitude needed, provided we know the transition width or T_2. For a transition with a moment of 3 D and a width of 1 cm^{-1}, $\epsilon \simeq 10^4$ V/cm or $\simeq 10^5$ W/cm^2, which nowadays can easily be achieved. If the radiated field is $10^{-3}\epsilon$, then the radiated power $\simeq 13$ mW/cm^2, a flux that can be detected by conventional detectors.

In the classical photon echo experiments on ruby by Hartmann and his group[4] pulsed lasers with high peak powers were used to generate the coherent polarization, and the generated field was probed by another pulse delayed in time. This allowed them to measure the loss of the polarization and hence the dephasing rate in ruby. Subsequently, continuous wave lasers were used; the laser was at fixed frequency and the molecule was tuned on- or off-resonance with the laser by using an externally applied electric field. Hence, in effect the molecules (which must be polar) can "see" light pulses of certain duration when the electric field is on for that duration and "see" no light when the applied electric field is turned off. The observation of the transients during the on and off periods permits one to measure T_2, as demonstrated clearly by Shoemaker and Brewer.[5] Several groups have since then observed a variety of transients in the microwave and IR regions. In 1973, instead of switching the molecule, Hall[6] frequency switched the laser—transients were observed for methane at 3.39 μm. Brewer's group[7] at IBM was successful in switching the frequency of a dye laser and had the sample in a different configuration, outside the laser activity. In our efforts[8] at Caltech, we have used a different method where the spontaneous emission at right angles to the laser is used to monitor coherent
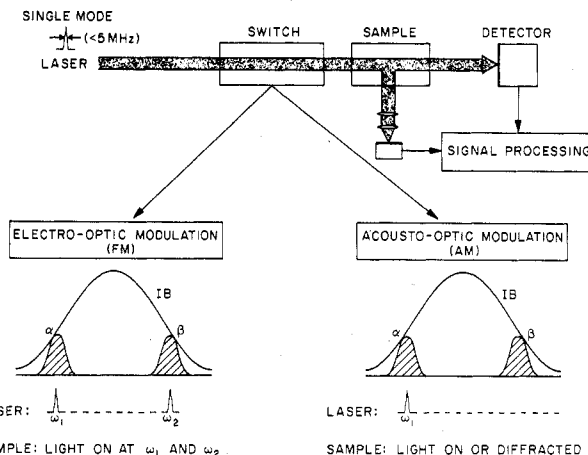
Figure 2. The figure illustrates the principles of coherent transient techniques. α and β are two distinct molecular "packets" or groups.

transients. Also, Orlowski et al.[9,10] have observed these transients by using an acoustooptic modulator outside the dye laser cavity. Optical transients of atoms in gases and ions in solids have been studied by the IBM group while our focus at Caltech has been on molecules in solids and beams.

The Method and the Transients

In Figure 2, the ideas behind the measurements of optical dephasing using a CW laser and a switch are depicted. A single mode laser (<5-MHz width) is used to excite coherently a homogeneous subgroup of molecules, say α of Figure 2. The laser is then either diffracted acoustically so it will no longer "see" the sample or switched into another frequency within the IB line (β of Figure 2). The $\pi/2$ and π pulses are made by controlling the diffraction duration time or the frequency switching time. Details of the experimental setup can be found in ref 11.

When the group of molecules α are excited coherently, the superposition of states discussed above will be established. As a result, a polarization is induced and if, e.g., the laser is suddenly turned off, a coherent burst of light, sometimes called superradiance,[2] can be detected. Several transients can be observed depending on the pulse sequence. These include photon echo, optical nutation, incoherent resonance decay, and optical free induction decay (OFID). The important point is that using these transients we can obtain T_1, T_2, and μ of the molecules involved. In what follows I shall describe the new findings obtained for molecules in different phases. Before going into the details, however, the meaning of these different transients will be explained.

If the α group of molecules is brought into resonance with a strong coherent optical field, the population can be completely driven from the ground state to the excited state in an oscillatory fashion as molecules alternately absorb and reemit radiation coherently (eq 9 and 10). This process, known as optical nutation, observed in gases[12] and solids,[13] has an oscillation fre-

(4) N. Kurnit, I. Abella, and S. Hartmann, *Phys. Rev. Lett.*, **13**, 567 (1964).

(5) (a) R. L. Shoemaker and R. G. Brewer, *Phys. Rev. Lett.*, **28**, 1430 (1972). (b) For a recent and thorough review, see R. L. Shoemaker in "Laser and Coherence Spectroscopy", J. Steinfeld, Ed., Plenum Press, New York, 1978.

(6) J. L. Hall, "Atomic Physics 3", S. J. Smith, G. K. Walters, and L. H. Volsky, Eds., Plenum Press, New York, 1973, p 615.

(7) R. G. Brewer and A. Genack, *Phys. Rev. Lett.*, **36**, 959 (1976).

(8) A. H. Zewail, T. E. Orlowski, and D. R. Dawson, *Chem. Phys. Lett.*, **44**, 379 (1976). For a review, see: A. H. Zewail, D. Godar, K. E. Jones, T. E. Orlowski, R. R. Shah, and A. Nichols, *Adv. Laser Spectrosc. I*, SPIE Pub. Co., Bellingham, **113**, p 42 (1977).

(9) T. E. Orlowski, K. E. Jones, and A. H. Zewail, *Chem. Phys. Lett.*, **54**, 197 (1978).

(10) A. H. Zewail, T. E. Orlowski, K. E. Jones, and D. Godar, *Chem. Phys. Lett.*, **48**, 256 (1977), and ref 9.

(11) T. E. Orlowski and A. H. Zewail, *J. Chem. Phys.*, **70**, 1390 (1979).

(12) B. Hocker and C. L. Tang, *Phys. Rev.*, **184**, 356 (1969). See also ref 5 for a review of subsequent work.

quency ω_R. A nutation is damped due to inhomogeneous and homogeneous dephasings. From this transient, which occurs at the leading edge of the laser pulse, one can measure T_2 and μ.[11]

OFID is a different transient. As a group of molecules initially on resonance with the laser (not necessarily a strong field) is suddenly switched off-resonance, they will emit initially in phase. If the laser is taken from group α to β, then the coherent emitted light by α molecules can beat against the new laser frequency (absorbed by the β molecules) and can be observed if a square-law detector is used for monitoring the transmitted laser beam. The beat pattern will decay as the molecules dephase and as with the optical nutation, the OFID contains contributions from inhomogeneous dephasings. Extrapolated to zero laser power gives the decay time T_2. OFID has been observed in gases,[14] beams,[15] and solids.[8,9,11,17]

In a photon echo experiment, one laser pulse is used to create a polarization. Then one waits for a period τ during which the macroscopic polarization is fanning out because of IB. At this instant τ a second pulse is applied to restore the polarization by refocusing it again. If one waits for an additional period τ, which is the time it takes the polarization of all molecules to rejoin, a burst of light, the photon echo, will be observed, as first demonstrated at Columbia by Hartmann and his group.[4] The echo in this case "travels" with the exciting laser beam ("stimulated" radiation) and decays by T_2. If, on the other hand, a third pulse is applied at time 2τ, the refocused polarization can be converted to a population and one sees the echo as a "hole" burned on the spontaneous and incoherent emission, as observed in iodine by Zewail et al.[10]

Finally, if the emission intensity is measured as the single-mode laser frequency rapidly changes from α to β, then one should see the superposition of two processes. First, α molecules will decay (by T_1) since they are now off-resonance. At the same time, β molecules are being driven coherently (i.e., nutating or ringing) by the laser field toward some equilibrium population distribution. Thus, as we shall see later, the observed signal will show an initial rapid buildup and nutation transient (β molecules) and a decay due to the α molecules. This transient was observed by Orlowski et al.[8,16] in iodine gas.

Optical Dephasing of Large and Small Molecules

Molecules in "Bulbs" and in Effusive and Supersonic Beams. In the bulb, collisional relaxation ensures that the system reaches equilibrium at long times. This means that the coherent excitation can be described by the density matrix equations of motion or by Bloch equations of a closed two-level ensemble

discussed in the previous sections. On the other hand, in beams because the molecules enter and leave the laser beam the population is flowing in an open system where the total number of molecules in the two levels is changing. This problem has been treated by Jones et al.[15] in order to extract the correct optical T_1 and T_2 from the transients.

Using the techniques described above we have observed the coherent transients of I_2 in bulbs and in effusive beams. We used the spontaneous emission and detected the photon echo,[10] the nutation,[16] the OFID, and the incoherent resonance decay, the IRD[8] (see Figure 3). Also, Lambert[18] has obtained the IRD of I_2 in a nozzle beam as a function of the vibrational energy. From these transients we obtained T_1, T_2, and μ and learned the following: (a) the collisionless beam[15] $T_1 = 1.24 \pm 0.02$ μs is in excellent agreement with the zero-pressure value of I_2 in the bulb; (b) the IRD of I_2 is in good agreement with the results of Lehmann and his group.[19] Due to predissociation the lifetimes change nonmonotonically as we excite the molecule to higher energies. For an excellent review see ref 19; (c) the natural width of the selectively excited X $^1\Sigma_g^+ \rightarrow$ B $^3\Pi_{o+u}$ rovibronic state at 5897.5 Å is 128 ± 2 kHz; (d) in the nozzle beam, the IRD gives $T_2 = 2.52 \pm 0.04$ μs, again consistent with a homogeneous width of 126 kHz; (e) the observed OFID in the beam shows that $T_2 \simeq 2T_1$, consistent with the expectation that T_2' is zero under collisionless conditions and in the absence of intramolecular dephasing; finally, (f) the cross section for collisional quenching from the IRD experiments is 64 Å, in agreement with the results of ref 19 and also with a recent theoretical analysis.[20] The similarity between our narrow-band excitation results and those obtained using a broad band indicates that iodine transitions are behaving like two-level systems with no unusual intramolecular processes.

From the above discussion it is clear that these techniques are quite valuable in providing information on collisional quenching, radiative broadening, dephasing, and most importantly in disentangling the IB of the optical transition. The following example illustrates the latter point. At 10-mtorr presence, the echo decay of Figure 3 provides the total homogeneous width; $\Delta\nu_H = 1/(\pi T_2) = 579$ kHz. The inhomogeneous width $\Delta\nu_I \simeq 1/T_2^* \simeq 400$ MHz. In other words, the HB is three orders of magnitude less than the IB. Furthermore, since we know the radiative T_1 (see eq 8) from the beam experiments, we can find the contribution of pure dephasing and collisionless quenching to the HB. At this pressure the optical HB is dominated (71%) by pure dephasing. Hence, we can now separate elastic and inelastic scattering events which must depend on the nature of the potential-energy surfaces.

Molecules in the Condensed Phase: Electronic Dephasing. Molecules in solid matrices (e.g., mixed crystals) are said to be isolated from the host influences.

(13) A. H. Zewail and T. E. Orlowski, *Chem. Phys. Lett.*, **45**, 399 (1977), and ref 11 for more details.

(14) R. G. Brewer and R. L. Shoemaker, *Phys. Rev. A*, **6**, 2001 (1972). For a discussion of a new class of OFID experiments, see the paper by M. S. Feld and his co-workers: *Phys. Rev. A*, **17**, 623 (1978).

(15) A. H. Zewail, T. E. Orlowski, R. Shah, and K. E. Jones, *Chem. Phys. Lett.*, **49**, 520 (1977); K. E. Jones, A. Nichols, and A. H. Zewail, *J. Chem. Phys.*, **69**, 3350 (1978).

(16) T. E. Orlowski, K. E. Jones, and A. H. Zewail, *Chem. Phys. Lett.*, **50**, 45 (1977).

(17) H. deVries and D. Wiersma, *J. Chem. Phys.*, **70**, 5807 (1979). An earlier report of the OFID was given in the Molecular Crystal Symposium meeting in Santa Barbara, CA, 1977.

(18) Wm. Lambert, unpublished results from this laboratory. In these experiments I_2 was seeded into a supersonic expansion of helium as was done first by R. E. Smalley et al., *J. Chem. Phys.*, **64**, 3266 (1976), to obtain the frequency resolved spectra. The transitions corresponding to 12–1 and 10–0 vibronic bands appear approximately at 16 923 and 16 901 cm^{-1}. The vibrational temperature is calculated to be 75 K, but the rotational temperature is ~0.4 K.

(19) J. C. Lehmann, *At. Phys.* **5**, 167 (1977).

(20) S. Mukamel, A. Ben-Reuven, and J. Jortner, *J. Chem. Phys.*, **64**, 3971 (1976).
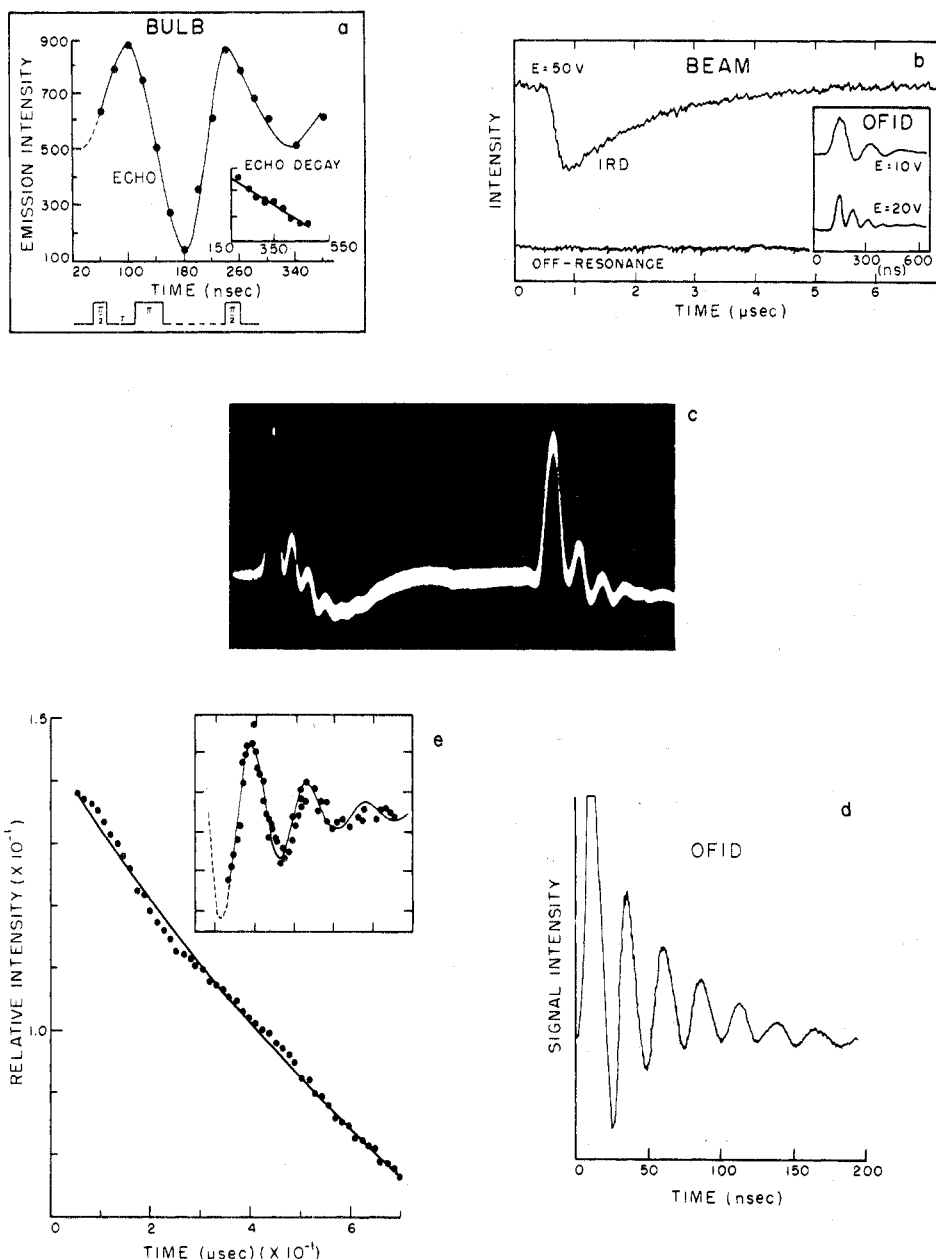
Figure 3. The different coherent transients observed in gases and beams of iodine: (a) the photon echo observed on the spontaneous emission;[10] (b) the IRD and OFID observed in an iodine beam;[15] (c) OFID and nutation of iodine gas observed by frequency switching a *ring* dye laser (Wm. Lambert, M. Burns, and A. H. Zewail, to be published); (d) the OFID of iodine gas observed by frequency switching a conventional dye laser; (e) the transient nutation of iodine gas detected on the spontaneous emission.[8,16]

However, phonons play an important role in the dephasing process, and it is, therefore, important to separate intra- and intermolecular relaxation processes. A molecule which we have studied in some detail is pentacene at low temperatures, 1.7 K and above. We have reported on the first observation[13] of optical nutation in a solid with large molecules. Subsequently, the OFID was observed.[8,11,17] The photon echo of this system was also observed by using pulsed excitation by Wiersma and this group.[21] Figure 4 shows the transients of this system, and the full details of the study are presented in ref 11. Several important conclusions have emerged from the study of the pentacene molecule.

The transition moment of the first singlet state of pentacene in *p*-terphenyl host was determined from the optical nutation to be 0.7 ± 0.1 D. At 1.7 K, $T_1 = 23.5$

ns and, as can be seen from eq 8, this means that T_2'-type processes are essentially frozen out. In other words, the total dephasing is due to spontaneous emission, as we observed in the T_2 beam experiments. At higher temperatures, phonons of certain energies (~ 20 cm^{-1}) accelerate the T_2'-type processes and (we shall see why later) make the optical dephasing very rapid: nanoseconds to picoseconds at high temperatures. When T_2' becomes relatively short there will be *no* apparent relationship between the lifetime of the state and the homogeneous linewidth of the transition.

In the pentacene system, the homogeneous width at 1.7 K is 7.1 ± 0.4 MHz, from the above T_2 measurements, while the inhomogeneous and apparent width of the 0,0 transition at this temperature is 2 cm^{-1}. If we had studied the temperature dependence of this IB resonance, the result would not have yielded the true effect of temperature on homogeneous dephasing.

(21) T. J. Aartsma, J. Morsink, and D. A. Wiersma, *Chem. Phys. Lett.*, **47**, 425 (1977); *Phys. Rev. Lett.*, **36**, 1360 (1976).
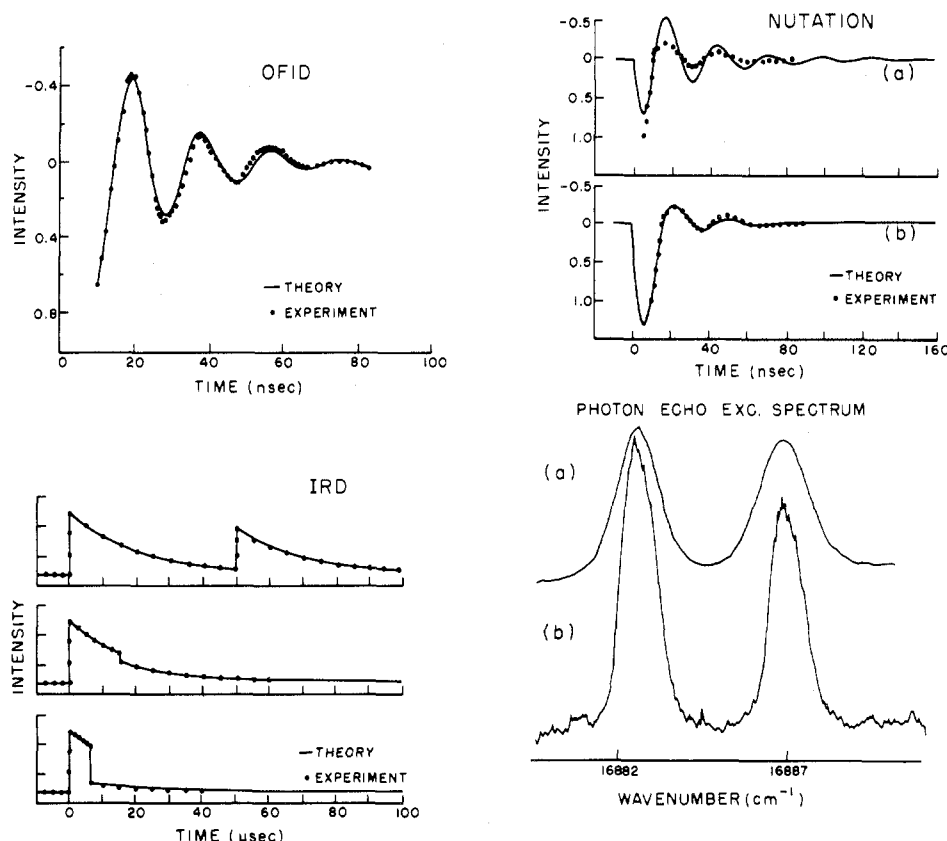
Figure 4. The different coherent transients observed in solids: pentacene in p-terphenyl at ~1.7 K. The OFID, the nutation, and the IRD at different pulse widths are taken from ref 11. The photon echo excitation spectrum is the courtesy of Dr. D. A. Wiersma. (Reprinted with permission from ref 21. Copyright 1976, American Institute of Physics.)

Even though the pentacene level structure (with 102 vibrations) is complicated by the many vibrational levels in quasi-resonance with the singlet state, the dephasing of the molecules can be handled[11] by using two time scales, the short (relative to T_2) and the long time scale where processes such as intersystem crossing may contribute to T_1 of the singlet state. At short times, pentacene behaves like an ideal two-level system. At long times, the coherence established in the two levels is lost to or averaged by nearby triplet states. In fact, observing the transients at long times allowed us to measure[11,22] the rate of intersystem crossing in pentacene, which depends on the host, as shown recently.[11,17,22] To account for dephasing in multilevel systems in a rather rigorous way, we have applied the Wilcox–Lamb method to pentacene. This allowed the separation of coherent and incoherent effects.[11]

Finally, even at 1.7 K, the dephasing of high-energy vibrational states in the excited singlet is much faster than that of the zero-energy level. For example, at 267 cm^{-1} above the zero-point level, T_2 = 5.4 ps.[11] More on the origin of these optical dephasing events will be discussed in the sections on theory to follow.

Vibrational Dephasing of High-Energy Vibrational Overtones. A great deal of attention has been focused recently on the origin of relaxation of molecules in vibrationally hot states, i.e., molecules with a high degree of excitation associated with "local" vibrational modes in the ground electronic state. These states presumably play an important role in the mechanistic description of processes such as multiphoton dissocia-

tion of molecules, laser isotope separation, and possibly selective laser-induced chemistry.

Studies of the energetics of these states have been done on molecules in liquids and gases.[23] We have chosen to study the overtones in low-temperature matrices (1.3 K) in order to obtain the dephasing and eliminate the contribution of thermal spectral congestion. Frequency-resolved spectra were used, since the apparent dephasing time is very short (<1 ps).

For naphthalene, Perry and Zewail[24] have found that the α- and β-CH stretches of the fifth overtone have different apparent dephasing times ($T_2{}^\alpha$ = 73 fs and $T_2{}^\beta$ = 0.11 ps). If this dephasing is dominated by T_1 processes, then we must conclude that the vibrational energy of the five quanta CH modes is "flowing" very rapidly to other modes. Interestingly, when we compare the results on naphthalene with those on benzene,[23] we find that the β dephasing time (and not α) appears to be comparable to the benzenic dephasing time. Furthermore, in molecules like durene, the relaxation time and the energies of methyl CH are different from those of aromatic CH. The results in Figure 5 for durene indicate that there are two different types of intramolecular baths for the CH to relax its energy. It also shows clear, narrower transitions for the aliphatic CH's even at v = 5 energy, the narrowest resonance (~20 cm^{-1}) observed so far in this high-energy overtone region! We will know the mechanism of coupling when

(22) Wm. Lambert and A. H. Zewail, *Chem. Phys. Lett.*, **69**, 270 (1980).

(23) For a review, see the articles by Albrecht and Reddy et al. in "Advances in Laser Chemistry", A. H. Zewail, Ed., Springer, Berlin, Heidelberg, New York, 1978.

(24) J. W. Perry and A. H. Zewail, *J. Chem. Phys.*, **70**, 582 (1979); *Chem. Phys. Lett.*, **65**, 31 (1979).
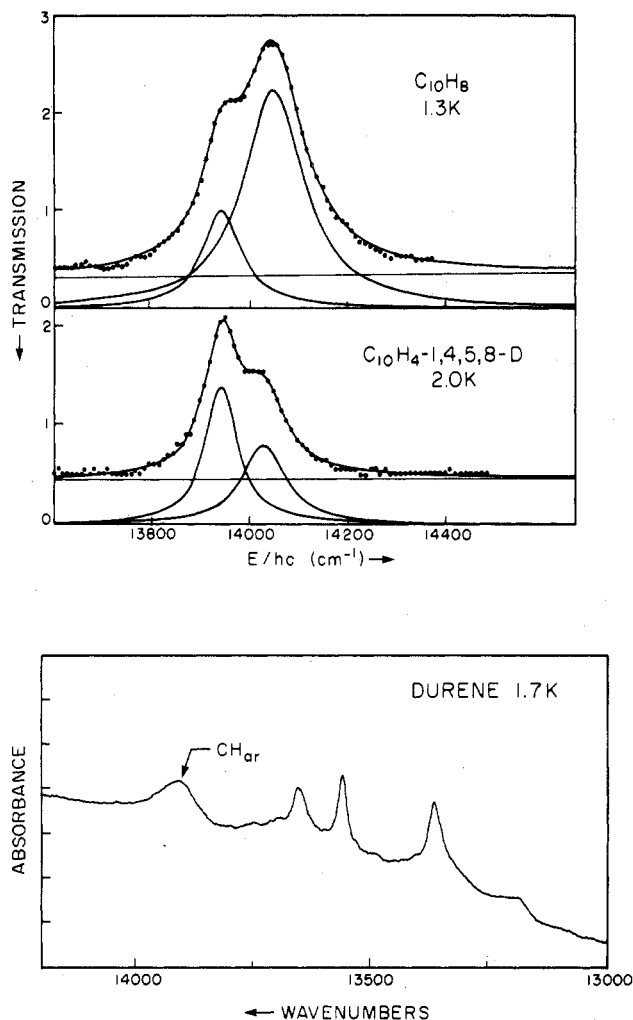
Figure 5. Top: The overtone $(0 \to 5)$ spectra of naphthalene-h_8 (1.3 K) and naphthalene-d_4 (2 K). The solid lines are the best computer fits, and the crosses are the digitized experimental data.[24] Bottom: The durene overtone spectrum at $T = 1.7$ K.

experiments on partially deuterated samples are completed. Perry is currently examining this problem.

Another technique for investigating overtone dephasing was reported recently by Smith and Zewail.[25] Smith observed emission to the overtones from high-energy electronically excited states. In contrast to absorption measurements, very small concentrations can be used (1 part in 10^6) and the detection sensitivity is quite high. In benzophenone we have located up to $v = 6$ of the ground state CO mode and measured the apparent width as a function of excitation energy. The apparent dephasing rate appears to be linear in the v energy in benzophenone. The latter is a very important finding because it might add to our understanding of the intermode coupling in the molecule, e.g., between the C=O and C—C bonds. Smith has now completed the line-width studies at different temperatures, and from these experiments we have learned that overtone relaxation is efficient, possibly due to the torsional modes of benzophenone. This would be an example of vibrational relaxation and dephasing due to forces imposed on the CO "oscillator" by neighboring bonds.

Dephasing of Collective Excitation (Excitons). If the laser excites a collection of molecules interacting with each other to form an exciton with a wave vector

(25) D. D. Smith and A. H. Zewail, *J. Chem. Phys.*, **71**, 540 (1979).

k, the dephasing of these excitons proceeds by exciton–phonon and exciton–impurity interactions in addition to the usual radiative (superradiance) effects. In effect, phonons and impurities scatter the exciton among the different **k** states of the solid. Hence, measurements of T_1 and T_2 provide direct ways for understanding the transport and scattering processes that might take place after the excitation. Magnetic resonance and line-shape analysis have been used to estimate T_2.[26]

Recently, Smith and Zewail[27] measured the *optical* dephasing due to **k**-to-**k′** scattering. We found that these dephasing events are slow at relatively low temperatures, microseconds. Furthermore, the **k**-to-**k′** scattering is not the sole dephasing channel for the laser-prepared exciton (**k** $\sim$ 0). While the T_2^* of the exciton is $\sim$5 ps, the **k**-to-**k′** scattering time is at least four orders of magnitude longer.

Theory of Optical Dephasing

Common to all the experiments discussed above one would like to know the answer to the following questions: What causes dephasing? Is it a microscopic effect?

To examine these questions in more detail, Jones and Zewail[28] and Diestler and Zewail[29] have provided a theory for vibronic dephasing of molecules in the condensed media (e.g., a molecule surrounded by lattice atoms). The theory (a) separates intra- from intermolecular effects and (b) separates dephasing by population loss from dephasing by phase relaxations.

In general, the rate of dephasing is given by eq 8, where the rate of pure dephasing can be expressed as follows:[28]

$$\frac{1}{T_2{}'} = \frac{\pi}{\hbar} \sum_p W_p \sum_{p'} |\langle ip|V|ip \rangle - \langle fp|V|fp \rangle|^2 \, \delta(E_p - E_{p'})$$

$$= \frac{\pi}{\hbar} \sum_p W_p \sum_{p'} |\langle p|\Delta V|p' \rangle|^2 \, \delta(E_p - E_{p'}) \qquad (13)$$

with $\Delta V = \langle i|V|i \rangle - \langle f|V|f \rangle$. In this expression, V is the potential describing the "scattering" of the molecules in the initial, i, and final, f, states by the phonons (external or internal vibrations) in states p and p'. The phonon probability of occupation is W_p. We immediately see that the T_2' is a dephasing time for an *elastic* process that conserves energy through the delta function $\delta(E_p - E_{p'})$. Because of this the molecule remains in the initial or final state and the process is called pure dephasing.

In ref 28 and 29, we separated the molecular properties of the potential energy surface (PES) determined by ΔV from the "lattice" effect described by p and p'. The full PES in a given electronic state i has in it the dependence of the dephasing on the internal coordinates, Q, of the molecule and the external lattice modes. Expanding around the equilibrium configuration of the lattice, we showed that the "cross section" for pure dephasing can be written as

(26) For a review, see: D. Burland and A. H. Zewail, *Adv. Chem. Phys.*, **40**, 369 (1979).
(27) D. D. Smith and A. H. Zewail, *J. Chem. Phys.*, **71**, 3533 (1979).
(28) K. E. Jones and A. H. Zewail in ref 23.
(29) D. J. Diestler and A. H. Zewail, *J. Chem. Phys.*, **71**, 3103, 3113 (1979).

$$\frac{1}{T_2'} = |\langle f|V_2(Q)|f\rangle|^2 \sum_{\mu,\nu} A_{\mu\nu}\bar{n}_\mu(\bar{n}_\nu + 1)\delta(\omega_\mu - \omega_\nu) \quad (14)$$

where $A_{\mu\nu}$ is a constant depending on all phonon modes μ and ν. It follows that two phonons are needed: absorption $\bar{n}_\mu$ and emission $\bar{n}_\nu + 1$, with $\bar{n}$ being the average phonon occupation number. $V_2(Q)$ is part of the full interaction potential that leads to pure dephasing but only depends on Q. After carrying out the sums in eq 14 for certain phonon density of states (e.g., a Debye solid), we obtain

$$T_2'^{-1} = A_R|\langle V_2(Q)\rangle|^2 T^7 \quad \text{(Raman-type dephasing)}$$
$$= A_a|\langle V_2(Q)\rangle|^2 e^{-\Delta/kT} \text{ (activaton-type dephasing)}$$
$$(15)$$

where A_R and A_a are constants for Raman and activation-type processes. Δ is the average energy of the phonons causing the dephasing. Other temperature dependences can also be obtained.[28,29]

Effect of Molecular Anharmonicity. An important point displayed by the above equations is the fact that pure dephasing cross sections depend on the nature of the molecular $V(Q)$ and in general on the disparity of the interaction in the initial and final states, i.e.,

$$\langle \phi_i\chi_i|V_2(Q)|\phi_i\chi_i\rangle - \langle \phi_f\chi_f|V_2(Q)|\phi_f\chi_f\rangle \quad (16)$$

Hence we can explain the conditions under which electronic (ϕ_i) dephasing is faster or slower than vibrational (χ_i) dephasing. In fact, we have performed quantum mechanical calculations[29] of these cross sections for impurity molecules (Cl_2) in a host lattice (argon) and found that dephasing depends on the vibrational quantum numbers involved in the optical transition, the shift in the equilibrium position on going to the excited state of the molecule, and the anharmonicity of PES. This can be seen easily if $V_2(Q)$ is expanded in Q. The influence of the linear and quadratic (in Q expansion) anharmonicity terms on dephasing is detailed in ref 29.

Overtone Dephasing. In eq 16, ϕ_i and ϕ_f will be identical for an overtone transition. Consequently, the dephasing of the different overtones will depend on $\langle \chi_i|Q|\chi_i\rangle - \langle \chi_f|Q|\chi_f\rangle$ and $\langle \chi_i|Q^2|\chi_i\rangle - \langle \chi_f|Q^2|\chi_f\rangle$, both of which can be evaluated, e.g., for a Morse potential. Doing so, we[29,30] found that the rate of dephasing increases quadratically with the vibrational quantum number (ν) but faster increase occurs if the surface is anharmonic, as in the case of, e.g., CH local modes. A homogeneous T_2'-type dephasing of 100 ps at $\nu = 1$ will be <1 ps for $\nu = 10$. On the other hand, for T_1-type dephasing the linear dependence (or close to it) will dominate since for a harmonic oscillator the matrix element for $\nu \pm 1$ to ν is proportional to $\nu^{1/2}$. These features of dephasing, if transferable to the subvibra-

tional space of large molecules, will be manifested in dephasing experiments on isolated molecules, as discussed before.

Spin vs. Orbital Dephasings. An interesting question was recently raised by the author:[31] Are the homogeneous line widths (or dephasing) of spin resonance and optical transitions related? This question is particularly relevant when one measures the optical dephasing of triplet states and compares the dephasing time with that obtained from magnetic resonance in the photoexcited triplet state.

As it turns out, spin–orbital coupling (SOC) leads to a correlation between spin and orbital dephasings. In the absence of SOC, there is no reason that every spin dephasing event will be accompanied by orbital dephasing. On the other hand, in the presence of SOC, these two scattering processes are interrelated and in certain limits spin dephasing may become the same as orbital dephasing.[31] Similarly, one can relate the *inhomogeneous* dephasing of spin and optical transitions through SOC.[32,33]

Epilogue

I wish to make several comments about the future. Because the field is in its infancy, more studies of different molecules under different conditions are desirable. This will improve our understanding of the origin of dephasing. Large molecules with complex level structure may exhibit different dephasing that simply probes different nonradiative processes in the molecule. Vibrational dephasing is also an important process for understanding the *selective* mode-to-mode couplings in large molecules. With the advances made recently in picosecond spectroscopy and single mode lasers, this field seems to promise survival with excitement, at least from my point of view.

(30) A. H. Zewail and D. J. Diestler, *Chem. Phys. Lett.*, **65**, 37 (1979).

(31) A. H. Zewail, *J. Chem. Phys.*, **70**, 5759 (1979).
(32) J. P. Lemaistre and A. H. Zewail, *J. Chem. Phys.*, **72**, 1055 (1980).
(33) J. P. Lemaistre and A. H. Zewail, *Chem. Phys. Lett.*, **68**, 296 (1979).