Time-Resolved Absorption Spectra of Dissociating Molecules

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We present a simple model of time-resolved absorption spectra of molecules that are in the process of dissociating. Within an "impact approximation," the spectra are shown to be superpositions of Lorentzian and dispersion profiles with relative weights determined by a net phase shift. New methods are proposed for obtaining molecular transition frequencies and relative transition dipole moments as functions of internuclear separation. Experimental data on TlI are compared to theoretical predictions, with good overall agreement.

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Using femtosecond laser pulses, it has become possible to take "snapshots" of elementary chemical processes and thus monitor reaction dynamics in real time.[1,2] Such experiments utilize a very short laser pulse to initiate a process, and a short probe pulse to monitor the time evolution of the system. For example, a laser pulse can be used to excite an initially bound molecule to a repulsive state. The dissociation process can then be monitored by probing a transition from the repulsive state to a higher state, as illustrated in Fig. 1. Real-time measurements of molecular dissociation have been carried out by groups at Caltech[1–4] and IBM.[5,6] A variety of other processes can be studied with femtosecond time-resolved spectroscopy by exciting molecules into bound or predissociating states.[1,2] In this Letter we consider only situations where pump-laser excitation leads to direct dissociation. Since dissociation of a molecule may be viewed as a "half collision," one would thus expect a fundamental connection to exist between time-resolved absorption spectroscopy of dissociating molecules and collision broadening of spectral lines.

In this Letter we discuss time-resolved absorption spectroscopy of dissociating molecules in terms of a simple but very useful model that is closely related to adiabatic descriptions of collision broadening.[7,8] We show that this model accounts for the important observed features of time-resolved absorption spectra. We also propose new methods by which one can, in principle, obtain molecular transition frequencies and relative transition dipole moments as functions of internuclear separation.

Consider a dilute gas probed with an ideal delta-function pulse $\mathbf{E}_p(t) \propto \hat{z} E_0 \delta(t)$. After the probe pulse passes through the sample, the total output field is the sum of the probe field and the field radiated by the polarization that the probe induces in the sample, $\mathbf{E}_{tot}(t) = \mathbf{E}_{in}(t) + \mathbf{E}_{rad}(t)$. The power spectrum $I(\omega)$ is the square of the Fourier transform of the total field. The probe field has a white spectrum; thus the frequency-dependent part of $I(\omega)$ is proportional to the real part of the Fourier transform of the radiated field. For example, if isolated atoms are excited by the delta-function probe, then the radiated field is a damped wave $\propto e^{-i\omega_0 t} e^{-\gamma t}$, where ω_0 is the atomic resonance frequency and γ is the decay rate. The real part of the Fourier transform of this radiated field gives the familiar Lorentzian absorption profile, $L(\Delta) = \gamma/(\gamma^2 + \Delta^2)$, where $\Delta = \omega - \omega_0$.

If a half collision is in progress at the time of excitation by the probe pulse, then the radiated wave will be affected. Now, it is usually the case that the effective duration of the half collision is much shorter than the characteristic decay time of the radiated field. Thus most of the radiation will be emitted long after the atoms have separated. This "postcollision" radiation has the characteristic transition frequency of separated atoms, ω_0, but it is shifted in *phase* due to the molecular interaction. Except for the brief time interval of substantial molecular interaction, the radiated field is $\propto e^{-i\eta} \times e^{-i\omega_0 t} e^{-\gamma t}$. The phase shift η is the time-integrated frequency shift caused by the molecular interaction:
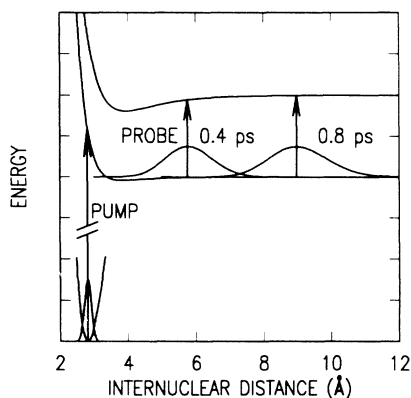

FIG. 1. Schematic diagram showing photodissociation of TlI by a 308-nm pump pulse, and time-resolved absorption monitored with a probe pulse. Distributions of molecules excited by the pump to the repulsive curve are shown for delay times of 0.4 and 0.8 ps, using a 160-fs FWHM pump pulse. The initial distribution of molecules in the ground-state potential well is also shown.

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$\eta = \int_0^\infty d\tau[\omega_m(\tau) - \omega_0]$, where $\omega_m(\tau)$ is the molecular transition frequency along a classical path $R(\tau)$. Using this damped, phase-shifted wave, the absorption spectrum, given by the real part of the Fourier transform of the radiated field, is thus $a(\Delta) \propto \cos(\eta)L(\Delta) + \sin(\eta)D(\Delta)$, where $L(\Delta)$ and $D(\Delta)$ are Lorentzian and dispersion profiles, $D(\Delta) = \Delta/(\gamma^2 + \Delta^2)$. The presence of a dispersion function accounts for the derivative-like appearance of the experimental spectra, shown in Fig. 2. The phase shift η also plays a key role in adiabatic treatments of collision broadening.[7,8] In particular, within the impact approximation, a collision can be regarded as suddenly shifting the phase of the radiator by an amount η. In the binary collision regime, steady-state collision-broadened lines have an approximately Lorentzian core, with a characteristic width and shift determined by η.

The impact approximation can be derived from a more general classical model of time-resolved absorption spectroscopy.[5,9] A brief description follows; a more detailed account will be published elsewhere.[9] The ideal probe pulse for time-resolved absorption studies would have an ultrashort duration and a broad bandwidth. In practice, broadband pulses spread out in time and develop a frequency chirp, due to propagation through dispersive optical elements. This results in a *frequency-swept* pulse, i.e., the average frequency varies smoothly from low to high optical frequencies.

FIG. 2. Time-resolved absorption spectra for TlI dissociated by a 160-fs pump pulse at 308 nm for frequencies near the Tl $6P_{1/2} \to 7S_{1/2}$ 377.6-nm transition. Experimental spectra (left panel) are compared to calculations (right panel) using the impact approximation, Eq. (2). Delay times for the calculations are shown on each spectrum, and the horizontal lines indicate zero absorbance.

Excitation by such a frequency-swept pulse is primarily due to a narrow time interval in which the probe frequency becomes resonant with the molecular transition frequency. This enables one to derive a simple expression for the macroscopic polarization that is induced by the probe. For a sufficiently weak probe, the induced polarization is linear in the incident probe field.[10] Absorption arises from interference between the field radiated by the induced polarization and the incident probe field. The change in spectral power density due to transmission through a sample of thickness dz is $dI(\Delta) = -a(\Delta)I_{in}dz$, where I_{in} is the spectral power density of the incident probe field. The absorption coefficient $a(\Delta)$ is given by[9]

$$a(\Delta) = \frac{8\pi^2}{\lambda}\frac{1}{V}\sum_k \text{Re}\left\{\frac{d_k(t^*)}{\hbar}\int_{t^*}^\infty dt\, d_k(t)e^{-\gamma(t-t^*)}\exp\left[i\left(\Delta(t-t^*) - \int_{t^*}^t d\tau\,\delta\omega_k(\tau)\right)\right]\right\}. \tag{1}$$

In this expression $\text{Re}\{\cdot\}$ indicates that the real part is taken; $\delta\omega_k(\tau) = \omega_m(R_k) - \omega_0$ is the frequency shift for molecule k traveling on the trajectory $R_k(\tau)$, t^* is the time that the probe is resonant with the molecular transition, and γ is the homogeneous damping rate. V is the volume of the sample that is probed, and the sum is over all of the molecules in V that have been excited to the repulsive state. Equation (1) applies if the probe sweep rate is much larger than the effective molecular sweep rate $\partial\omega_m/\partial t$. The general case of finite probe sweep rate is discussed in Ref. 9. Equation (1) can be evaluated using an "impact approximation," in which radiation emitted during the collision is neglected. The transition dipole moment $d(t)$ and the phase integral $\int_{t^*}^t d\tau\,\delta\omega_k(\tau)$ reach their asymptotic $(t \to \infty)$ values within a collisional time scale T_c. If γT_c and $|\Delta|T_c$ are both small, then one can approximate $d_k(t)$ by the separated-atom value d_0, and the phase integral by $\eta_k = \int_{t^*}^\infty d\tau\,\delta\omega_k(\tau)$. Equa-
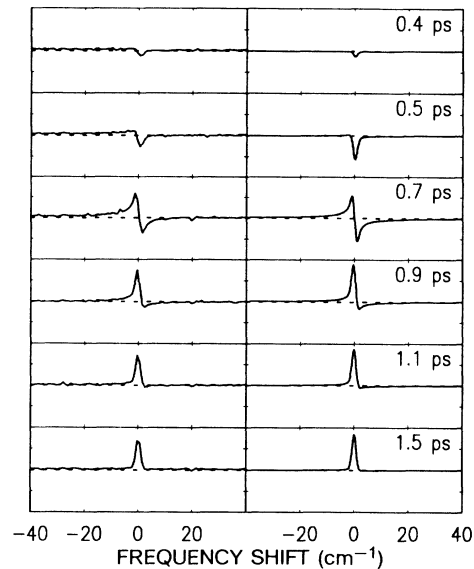
tion (1) then reduces to

$$a(\Delta) = \frac{8\pi^2}{\lambda}\frac{1}{V}\sum_k \frac{d_k(t^*)d_0}{\hbar}\{\cos(\eta_k)L(\Delta) + \sin(\eta_k)D(\Delta)\}. \tag{2}$$

For frequencies near the separated-atom resonance, the absorption spectrum is thus a weighted sum of Lorentzian and dispersion profiles, with weights that depend on phase shifts η_k. Corrections to this approximation[9] are often small for $|\Delta| \lesssim 10$ cm^{-1}.

The discussion above suggests a new method that can be used to obtain the molecular transition frequency as a function of internuclear separation R. If the dissociation process yields a narrow spatial distribution on the repulsive curve, then all of the molecules will contribute with essentially the same phase shift, which can be deter-

mined from the absorption profile by fitting with a superposition of Lorentzian and dispersion functions, as described above. Once the phase shift is known as a function of delay time, the frequency shift can be obtained by differentiation: $\delta\omega(t) = -\partial\eta/\partial t$. If the relationship between delay time and internuclear separation is known, then $\delta\omega(R)$ is determined. By analyzing numerically generated profiles based on Eq. (1), we have shown that this method accurately recovers $\delta\omega(R)$ from the spectra if the spatial distribution of molecules on the repulsive curve is sufficiently narrow.[9]

Equation (1) yields an important sum rule for the frequency-integrated absorption:

$$\int d\Delta\, \alpha(\Delta) = \frac{8\pi^3}{\lambda} \frac{1}{V} \sum_k \frac{|d_k(t^*)|^2}{\hbar} . \tag{3}$$

The frequency-integrated absorption is always positive, and it is proportional to the square of the transition dipole moment at the time of excitation by the probe pulse. This result can be used to obtain relative strengths of the transition dipole moment as a function of R, averaged over the wave packet at the time of excitation by the probe. We should point out that the classical model, Eq. (1), is closely related to the quantum-mechanical theory given by Lee, Pollard, and Mathies.[11] The quantum-mechanical treatment also yields a sum rule analogous to Eq. (3). The relationship between our classical model and other treatments of time-resolved absorption is discussed in Ref. 9.

We now consider time-resolved absorption spectra of TlI.[5] Ground-state molecules at $T \approx 670$ K are excited to a repulsive state using a 160-fs FWHM pump pulse at 308 nm. The resulting distribution of photofragments is probed with a frequency-swept continuum pulse, with a bandwidth of ≈ 20000 cm^{-1} and a sweep rate of ≈ 1340 cm^{-1}ps^{-1}. After transmission through the sample, the spectral power density of the output beam is measured with a spectrometer and an optical multichannel analyzer, with a resolution of ≈ 1 cm^{-1}. Time-resolved absorption spectra for frequencies near the Tl $6P_{1/2} \to 7S_{1/2}$ 377.6-nm transition are shown in Fig. 2 as a function of pump-probe delay. The absorption signal is always centered near the transition frequency for separated atoms. At large delay times the spectra approach a normal absorption profile for isolated Tl atoms. However, when the Tl and I atoms are interacting at the time of probe excitation, the spectra have a dispersion-like character.

The TlI system is well suited for theoretical analysis. Photofragmentation studies[12] show that a single dissociative state is excited by the 308-nm pump pulse. Time-of-flight data[12] and uv absorption spectra[13] provide information about the repulsive potential in the region near the ground-state potential well. One can approximately model the dissociative potential as a repulsive exponential, with a weak van der Waals well. The distribution of molecules excited to the repulsive curve can

then be calculated by classical trajectory methods. Results are shown in Fig. 1 for delay times of 0.4 and 0.8 ps, using a 160-fs FWHM sech^2 pump pulse. The calculated distributions are rather broad primarily because of the gradient of the repulsive potential over the width of the initial distribution.

Experimental absorption spectra are compared in Fig. 2 to calculations based on the impact approximation, Eq. (2). The absolute zero of the experimental delay-time scale was not known; thus we have shifted the data by a fixed delay time, which was chosen to approximately match the calculated spectra. The width of the "wave packet" plays a key role in determining the nature of the absorption spectra.[9] At small delay times (i.e., small internuclear separations), the phases η_k vary rapidly across the distribution of molecules that are excited by the probe. This results in destructive interference of the radiated waves; i.e., the sum over k in Eq. (2) tends to zero. Thus the spectra appear to "grow in" after a substantial delay time (~ 0.4 ps), when the wave packet has moved out to the van der Waals region, where phase shifts are small. The present calculations use $\sim 10^5$ trajectories to account for the distribution of molecules, and damped van der Waals potentials[14] to describe the two states that are coupled by the probe. Since the polarizability and ionization potential of atomic I are close to those of Xe, the C_6 coefficients were taken from the analogous states of TlXe.[15] Because of the interference effect mentioned above, the spectra near ω_0 are not sensitive to the details of the short-range potentials—only information about the long-range behavior is retained. If one attempts to describe the dissociation process by a single classical path, it is still possible to choose a difference potential to approximately match the data.[5] However, the resulting "potential" is not physically meaningful—a maximum frequency shift of ~ 30 cm^{-1} is required, and this value is at least 1 order of magnitude smaller than the frequency shift that would result from van der Waals interactions alone. Thus it is essential to include a distribution of trajectories. The experimental spectra show a slight enhancement in the absorption strength for delay times ~ 0.7 ps. Within our model, this can be accounted for by assuming that the transition dipole moment at $R \sim 6$ Å is enhanced by $\sim 50\%$ compared to the separated-atom value. However, the experimental enhancement depends on the intensity of the pump beam, with larger enhancements at higher intensities. The data shown are for the smallest intensity that we can use, and still have adequate signal-to-noise ratio. We suspect that in the limit of low pump intensities, the data would be consistent with a constant transition dipole moment over the van der Waals region.

In summary, we have presented a simple adiabatic model for understanding femtosecond time-resolved absorption spectra of molecules that are in the process of dissociating. In a close analogy to steady-state collision broadening, the dissociative half collision can often be

regarded as suddenly shifting the phase of the radiated field. However, in the time-resolved case there are two important new features: (1) The effect of the collision on the absorption spectrum begins at the point of excitation by the probe pulse, when the wave packet on the repulsive potential is more or less localized to some internuclear separation R^*; and (2) the net phase shift appears explicitly in the absorption profile via relative weights of Lorentzian and dispersion terms. If the wave packet produced by photodissociation is narrow, one can obtain the molecular transition frequency versus time from the dependence of the phase shift on pump-probe delay. If the wave packet is broad, as is the case for TlI, then interference limits the phase-shift information to long-range interactions.

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