Is Multiphoton Dissociation of Molecules a Statistical Thermal Process?

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We present here a phenomenological model calculation that exhibits the realistic qualitative behavior of multiphonon excitation and dissociation of polyatomic molecules. It is also used to show that at least theoretically multiphonon excitation of molecules is not equivalent to thermal heating.

There is at present a lively discussion concerning the dynamics of infrared multiphoton dissociation (MPD) of polyatomic molecules.[1] Recent molecular beam experiments have convincingly shown that in the many molecules investigated, the excitation energy in a molecule is completely randomized in all its vibrational modes before it is decomposed, and a statistical theory can be used to adequately describe the dissociation dynamics.[2] But there is another very interesting question that is worth pursuing: For an ensemble of isolated molecules under multiphoton excitation, what is the population distribution among the molecular energy levels? It has recently been proposed by Bloembergen and co-workers[3] that such a distribution can be considered as a thermal one characterized by an effective vibrational temperature which increases with laser pumping. One may, however, intuitively expect that there is a fundamental difference between monochromatic laser excitation and thermal heating. In thermal heating, which carries the assumption of adiabaticity, the molecules are always infinitesimally close to thermal equilibrium. However, this is not the case for laser excitation. We have recently developed a realistic model calculation of laser multiphoton excitation and dissociation of a molecule. This calculation describes the observed qualitative behavior of MPD very well. In what follows, we present some of these results. We also show a comparison of the laser-excited distribution with the thermally heated distributions and state the reasons for their discrepancies.

In their recent experiment, Black *et al.*[3] measured both the dissociation yield and the average number of infrared photons absorbed per molecule under multiphoton excitation. In order to minimize the effect of molecular collisions, they used subnanosecond laser pulses for excitation. They then suggested that multiphoton laser excitation could be considered as a statistical thermal process and their results could be interpreted by a simple theory describing such a process. They made the following assumptions in their theoretical calculation: (1) Multiphoton laser excitation is equivalent to thermal heating. (2) All the vibrational modes are degenerate. (3) The excitation energy in a molecule is randomized in all vibrational modes and the classical equipartition theorem is valid. (4) The dissociation rate is described by the quantum Kassel theory for unimolecular dissociation. Together with the thermal population distribution, it leads to the dissociation yield. (5) The thermal population distribution is not significantly perturbed by molecular dissociation.

Although their theoretical calculation is attractively simple, the assumptions are not easily justifiable. We present here a phenomenological model where many of the above assumptions can be eliminated. In our model calculation, we assume that the multiphoton excitation of a molecule can be described by stepwise incoherent one-photon transitions among a set of equally spaced energy levels; the degeneracy factor of each level is given by the corresponding molecular density of states which can be calculated. The excitation is then governed by the following set of rate equations:

$$dN_m/dt = C_{m-1}{}^a N_{m-1} + C_m{}^e N_{m+1} - (C_m{}^a + C_{m-1}{}^e)N_m - K_m N_m. \quad (1)$$

Here, N_m is the population in the mth excited level, and K_m is the molecular dissociation rate from the mth level calculated from the Rice-Ramsberger-Kassel-Marcus statistical theory for unimolecular dissociation.[4] (For levels below the dissociation energy E_0 we have $K_m = 0$.) $C_m{}^a$ and $C_m{}^e$, are, respectively, the absorption rate from level m to $m+1$ and the emission rate from $m+1$ to m. For one-photon transitions, we

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can write

$$C_m^{\,a} = \sigma_m I/h\nu, \quad C_m^{\,e}/C_m^{\,a} = g_m/g_{m+1}, \tag{2}$$

where σ_m is the absorption cross section for the m to $m+1$ transition, $h\nu$ is the photon energy, I is the laser intensity, and g_m is the degeneracy factor for the mth level. In the above model, we have ignored the initial one-step multiphoton transition over the discrete states. The calculation is therefore only valid when the laser intensity is much higher than the threshold intensity necessary to overcome the discrete-state barrier, e.g., ~30 kW/cm^2 for SF_6.[5] In the case of an exciting laser pulse with a long but weak leading edge, this calculation will overestimate the number of photons absorbed and yield an apparently lower laser fluence threshold for dissociation.[6] We also believe that the coherent effect in the present multiphoton excitation process is not important as long as the exciting laser pulse is longer than 10 nsec.

For a given molecule with σ_m and $I(t)$ specified, the set of rate equations in Eq. (1) can be easily solved on a computer. We have performed such a calculation using SF_6 as an example. The frequencies of the vibrational modes of SF_6 are well known. To find the densities of states, we used exact count at low energies and the Whitten-Rabinovitch formula at higher energies.[4] The dissociation energy E_0 was chosen to be 78 kcal/mole. The spacing between adjacent levels is 944 cm^{-1}. Because of anharmonic coupling among vibrational modes, the absorption cross section σ_m was expected to decrease with increase of m.[3,7] We assumed that σ_m takes the form

$$\sigma_m = \exp[\alpha m + \beta], \tag{3}$$

where $\alpha = -0.029$ and $\beta = -42.9$ for σ_m in cm^2. These values were chosen so that our numerical results fit the experimentally observed variation of the average number of photons absorbed[3] and the dissociation yield[8] as a function of laser energy fluence.

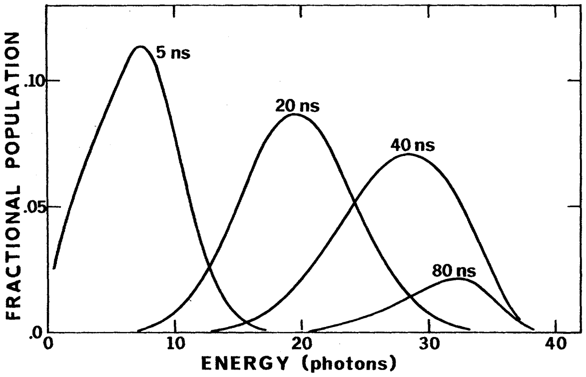

FIG. 1. Population distribution at various times produced by a 100-nsec rectangular laser pulse excitation of 200 MW/cm^2.

Figure 1 shows the population distribution at various times calculated with these parameters for a 100-nsec 200-MW/cm^2 rectangular laser pulse excitation. Initially only the ground level is populated, but the laser excitation, being a stochastic process, soon distributes the population over many levels. As time goes on, the population is continuously pumped up and the distribution curve shifts to higher energies. Correspondingly, the average excitation energy, $\langle n \rangle h\nu$, also increases with time. At $t \sim 20$ nsec, the high-energy tail of the distribution curve clearly extends beyond the dissociation level. We should then expect the onset of molecular dissociation. As the laser excitation continuously drives the population distribution upward, the dissociation yield increases rapidly. For those levels well above E_0, the depletion of their population is dominated by the dissociation rate. Consequently, the further up-excitation of the population is restricted, the population at the high-energy tail is heavily depleted by dissociation, and the distribution curve becomes asymmetric. The $t = 80$ nsec curve in Fig. 1 clearly exhibits this feature.

Our model also allows us to calculate the dissociation yield as a function of time. More specifically, we can calculate the dissociation yield per unit time, $Y_m(t) = K_m N_m(t)$, from each m level above E_0. In Fig. 2, we show the integrated dissociation yields from each level during and after the laser pulse. The total dissociation yield is of course the sum of all. As shown in Fig. 2, most of the molecules dissociate during the laser pulse. (More than half dissociate before $\frac{2}{3}$ of the laser pulse is over.) They dissociate mainly from those levels $(6-11)h\nu$ above E_0. These results are fairly consistent with the experimental observations. In particular, we can now understand why SF_6 will undergo a two-step dissociation process if the exciting laser pulse is sufficiently long and intense.[2] In the primary dissociation of SF_6 into SF_5 and F, our molecular beam experiment[2] has shown that, on the average, less than $h\nu$ of the total excess energy appears as recoil energy of the fragments; the rest is retained by SF_5 in its internal degrees of freedom. With the total excess energy $\gtrsim 6h\nu$, this puts SF_5 in the excited quasicontinuum states. Then, if the laser field

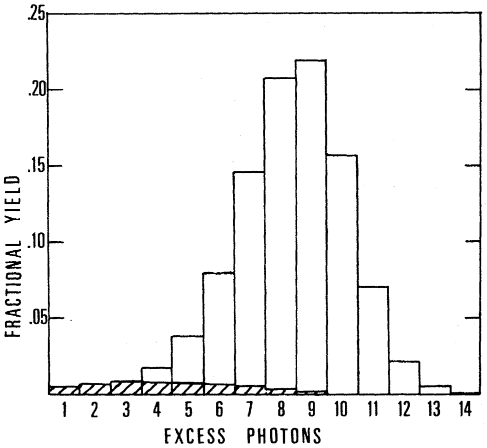

FIG. 2. Calculated dissociation yields from various levels above the dissociation energy during the laser pulse (unshaded region) and after the laser pulse (shaded region) for a 100-nsec, 200-MW/cm^2 laser pulse excitation.

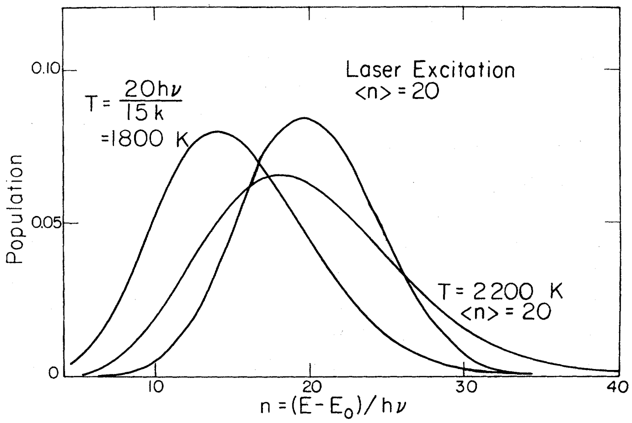

FIG. 3. Comparison of a laser-excited population distribution with $\langle n\rangle = 20$ with two thermal distributions: one with $T = 2200$ K corresponding to $\langle n\rangle = 20$ and the other with $T = 1800$ K obtained from the equipartition theorem $T = 20h\nu/15k$.

is still present for a sufficiently long time, the SF_5 fragments can readily absorb additional photons to exceed the threshold for subsequent dissociation into $SF_4 + F$. Apparently, this can happen for the case shown in Fig. 2.

We now turn to the question of how the laser-excited population distribution compares with a thermal distribution. This is shown in Fig. 3. The laser-excited distribution curve with $\langle n\rangle = 20$ was obtained from our model calculation at $t \simeq 20$ nsec. The thermal distribution with $T = 2200$ K has an average excitation energy of $\langle n\rangle h\nu \cong 20h\nu$, while the other with $T = 1800$ K has its characteristic temperature obtained from the equipartition theorem $15kT = 20h\nu$. To be more realistic, we have calculated the thermal distributions from the Boltzmann function

$$P(n) = Ag_n \exp(-nh\nu/kT), \qquad (4)$$

where A is a normalization constant and g_n is the realistic density of states used in Eq. (2). The correspondence between T and $\langle n\rangle$ can be easily calculated and is listed in Table I. We note that if we assume, as did Bloembergen and co-workers,[3] that the equipartition theorem $\langle n\rangle h\nu = skT_{\text{eff}}$ with $s = 15$ holds, then for a given $\langle n\rangle$, the "temperature" T_{eff} obtained is too low. In other words, the thermal distribution characterized by T_{eff} populates a significantly lower set of energy states than the real distribution characterized by $\langle n\rangle$. An example is shown in Fig. 3. The discrepancy here arises because the condition $kT \gg h\nu_i$ cannot be satisfied by several of the fifteen vibrational modes of SF_6 so that the classical equipartition theorem is not valid.

The above discussion suggests that it is probably more meaningful to compare the laser-excited distribution with the thermal distribution characterized by the same excitation energy $\langle n\rangle h\nu$. One finds that the thermal distribution is still broader and has a longer high-energy tail. One might expect that in a real situation, a smooth laser pulse may broaden the laser-excited distribution since the population must be "switched" into the quasicontinuum over a finite period. We have actually carried out a calculation assuming a Gaussian laser pulse and a three-photon transition across the discrete-state barrier into the quasicontinuum and found essentially no change in the $\langle n\rangle = 20$ laser-excited distribution. There is also no significant change if we assume that the population (normalized to 1) is switched into the quasicontinuum

TABLE I. Corresponding values of T, $\langle n\rangle$, s', and T_{eff}, assuming thermal distributions, $s' = \langle n\rangle h\nu/kT$, and $T_{\text{eff}} = \langle n\rangle h\nu/ks$ with $s = 15$.

T (K)	$\langle n\rangle$	No. of effective modes of s'	Effective temperature, T_{eff}
1600	12.8	10.9	1160
1800	15.2	11.5	1377
2000	17.5	11.9	1585
2200	19.6	12.1	1776
2400	21.7	12.3	1966
2600	23.6	12.3	2138

at a constant rate of 0.05/nsec. This is generally true in the case where the dissociation yield depends mainly on the laser energy fluence but not on the laser intensity. In fact, the thermal distribution can be approximated only if σ_m in the calculation remains constant or increases slightly with m. We can thus conclude that the thermal distribution is only a rather crude approximation to the laser-excited distribution. Experimentally, this can be verified by an accurate measurement of the dissociation yield, as well as $\langle n \rangle$, versus the laser energy fluence. Recent studies on intramolecular isotope effect in CH_2DCH_2Cl by Colussi, Benson, and Hwang indicated that the excitation energy distribution is indeed narrow.[9] At large dissociation yield, the laser-excited distribution being strongly affected by the fast dissociation will certainly be different from the thermal distribution.

In summary, we have shown that our phenomenological model calculation gives a realistic description of multiphoton excitation and dissociation of polyatomic molecules. Furthermore, it is used to demonstrate that multiphoton laser excitation is not really equivalent to thermal heating.

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Effects of Electric Fields upon Autoionizing States of Sr

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We report the first observation of significant perturbations by external fields of the autoionizing resonance structure of a two-electron atoms. The effects of electric fields up to 20 kV/cm on autoionizing resonances in Sr I were observed by three-photon ionization spectroscopy in an atomic beam. In addition to effects analogous to those for bound Stark states of a one-electron Rydberg atom, we observed a new effect: The characteristic shapes and widths of autoionizing resonances (Fano-Beutler profiles) can be strongly influenced by electric fields.

The occurrence of autoionizing (AI) resonances above the first ionization limit of atomic systems with more than one optically active electron has been the subject of theoretical[1] and experimental[2] investigation for years. Interest in AI states in general, and two-electron AI states in particular, has grown recently with the development of multichannel quantum-defect theory[3] and the experimental techniques of nonlinear sum-frequency generation[4] and multiquantum ionization spectroscopy.[5]

Previously, only the energies and characteris-

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