Mechanism of collisionless dissociation of molecules in the strong field of an IR laser

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A new mechanism is proposed for collisionless dissociation of polyatomic molecules in a strong IR-laser field; this mechanism takes into account the possibility of cancellation of the anharmonicity of the oscillations as a result of conversion of an appreciable fraction of the vibrational energy of the molecule into rotational energy.

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Since the publication of the reports[1] of observation of collisionless dissociation of molecules in the strong field of an IR laser, many attempts were made to explain the mechanism of this phenomenon. The main idea of the explanation consists in the following. During the first stage, the anharmonicity of the oscillations is overcome either by the large field amplitude,[2] or on account of its partial compensation by the change of the rotation energy (combination of P, Q, and R transitions[3,4]). The molecule then turns out to be in the region of energies with high density of the vibrational states, in which quasi-resonant transitions are always possible, and it is this which ensures the rapid excitation of the molecule.

While the treatment of the first state of the excitation has been analyzed in detail, the mechanism of the transitions in the quasi-continuous spectrum has not yet been explained. Formal estimates of[3,4] yield for the density of states high values (in a scale determined by the field broadening) already in an energy region corresponding to three or four absorbed quanta. But the high density is due mainly to the fact that substantially different vibrational states, most of which play practically no part in the interaction with the radiation, have the same energy. Near equality of the energy still does not guarantee a strong mixing of the harmonic-approximation states, since the interaction between them decreases rapidly with the increasing differences between the sets of the vibrational quantum numbers that characterize these states. The possibility of the interaction is also strongly restricted by differences between the sym-

metries of the states. Therefore their high density does not explain the mechanism whereby the molecule is excited at high energies.

The mechanism proposed in this paper is that of laser photodissociation of molecules with degenerate modes, with account taken of the possibility of the conversion of an appreciable fraction of the excitation energy into rotational energy, explaining by the same token the rapid quasiresonant excitation of the molecule at high energies. This possibility does not depend on the interaction between different vibrational modes and is caused by spectrum singularities connected with a degeneracy which is not accidental. These singularities are discussed below with octahedral-symmetry molecules, such as SF_6 as an example.

Neglecting all oscillation modes except the triply degenerate mode 3 which is active in the IR spectrum, we assume that the potential energy of the molecule can be roughly represented in the form $U = U_0 + \frac{1}{2} m \omega^2 (r^2 - \alpha r^4)$, where $r^2 = q_1^2 + q_2^2 + q_3^2$; q_1, q_2, q_3 are normal coordinates. Then the energy levels are characterized by the vibrational number v and by the value of the vibrational angular momentum $l = v, v - 2 \cdots 0$ or unity. In the first perturbation-theory approximation that follows the harmonic approximation we have

$$E_{v,l} = \hbar \omega \left[\left(v + \frac{3}{2}\right)^2 - \frac{3}{2} \alpha \left(v + \frac{3}{2}\right)^2 + \frac{1}{2} \alpha l (l + 1) - \frac{3}{8} \alpha \right] . \tag{1}$$

Violation of the spherical symmetry in potential energy and the Coriolis interaction lead to a total splitting of the degenerate levels (1), without changing substantially the width of the multiplet and the density of the levels in it. Almost all the states of the multiplet v are coupled via dipole transitions to almost all the states of the neighboring multiplets $v \pm 1$, and this coupling, generally speaking, is not weak. All that remains in force are the hindrance rules connected with the symmetry of states, which decrease negligibly the number of allowed transitions, while the restrictions on the change of l and other restrictions are listed.

An analysis of expression (1) shows that, starting with $v = 4$, the distance between the lower level of the multiplet v and the upper $v + 1$ is larger than $\hbar \omega_{10}$. A quasi-resonant excitation of arbitrarily high vibrational levels by a field of frequency close to ω_{10} is therefore possible if a mechanism exists that ensures rapid transitions from the upper levels of the multiplet to its lower levels. Qualitatively, the migration of the molecule over the levels of the multiplet v can be represented as a sequence of two-photon transitions that are resonant, accurate to $(2\rho)^{-1}$ (ρ is the density of the levels in the multiplet), for example $V_v, j \rightarrow V_v'', j + 2$, via the intermediate states $V_{v-1}', j + 1$ of the multiplet $v - 1$ (the subscript v of V_v indicates that the state pertains to the multiplet v). If the light is circularly polarized, this channel is less effective, but the following is possible $V_v, j \rightarrow V_{v-1}', j + 1 \rightarrow V_v'', j + 1$, etc. Such transitions can be induced in principle also by a field that is essentially nonresonant in the intermediate states, but is strong, although the rate of the transitions is decreased in this case. However, if the deviation of the strong-field frequency from resonance is not too large, such transitions become resonant also for the intermediate states V_{v-1}' in the region of high multiplets whose widths exceed this detuning. (These transitions are practically always quasi-resonant with a field of frequency ω_{10}).

Dropping to a sufficiently deep level of the multiplet v, the molecule absorbs

a quantum quasiresonantly and goes over to one of the levels lying at the upper boundary of the multiplet $v + 1$. The anharmonicity of the oscillations is thus completely cancelled out by the change of the rotational energy.

A quantum-mechanical analysis of the photodissociation process, as the only multiphoton process whose mechanism is described above, yields the following value for the threshold intensity

$$I_{thr} = \frac{v_{thr}}{g_0} I_0 ; \quad I_0 \approx \frac{3C}{50\pi^3} \frac{(\hbar\omega_{10} - \hbar\omega_{21})^2}{d_{01}^2} \quad , \tag{2}$$

where v_{thr} is the number of the level v_3 from which the predissociation takes place $(v_{thr} \gtrsim 40$ for $SF_6)$, $g_0 = (v_2 + 1)(v_4 + 1)(v_4 + 2)(v_5 + 1)(v_5 + 2)(v_6 + 1)(v_6 + 2)/8$ is the degeneracy factor and takes into account the difference of the vibrational numbers $v_{i \neq 3}$ from zero in the initial state, c is the speed of light, and d is the dipole moment. For SF_6 we have $J \approx 30$ MW/cm^2 $(d_{01}^2 \approx 10^{-37}$ cgs esu and $\hbar\omega_{10} - \hbar\omega_{21} \approx 2.9$ cm^{-1} [4]). Qualitative estimates based on the use of (2) are in reasonable agreement with the experimental data.[5] A check on the qualitative structure of this relation can be based on an investigation of the threshold properties and the rates of the laser photodissociation as a function of the temperature, and a check on the mechanism as a whole can be based also on an investigation of the dependence on the polarization characteristics of the radiation. We note also that in the case of low-symmetry molecules, an anharmonicity-cancellation mechanism similar to that described above is possible only on account of accidental degeneracy of the vibrational states. Therefore the threshold intensities for the dissociation of such molecules must be higher than for highly-symmetrical molecules having the same number of atoms.

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