Mechanism of collisionless dissociation of polyatomic molecules in a high-power laser beam

V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and L. A. Shelepin

P. N. Lebedev Physics Institute, USSR Academy of Sciences

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A theoretical analysis is made of the possible mechanism of collisionless (instantaneous) dissociation of molecular gas following resonant action of high-power laser radiation. It is assumed here that the excitation of the lower vibrational levels is due to allowed transitions, and that the detunings due to the anharmonicity of the vibrations are offset by the level broadening in the strong laser field. Further excitation of the molecules, all the way to the dissociation limit, is due in general to forbidden transitions in a quasicontinuous sequence of levels. It is established that the dependence of dissociation on either the intensity or the transmitted radiation energy has a threshold. The obtained estimates agree with the experimental data.

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The excitation of the higher vibrational levels of molecules by IR laser radiations of great interest in view of the ensuing possibility of initiating chemical reactions (see, for example, the review [1]). Nonthermal action of high-power laser radiation on molecular gas was first observed in [2]. Stationary irradiation of a gas whose molecules have a vibrational spectrum that coincides with the frequency of the laser radiation has led to a difference between the vibrational temperature and the translational temperature and to dissociation of the molecules. An essential role was played in this process by collisions which could simultaneously lead, generally speaking, to loss of selectivity of excitation of the molecules.

Somewhat later, a number of workers [3,4] have observed and investigated the so-called instantaneous dissociation of molecules, which is produced by pulsed excitation of resonant gases within a time much shorter than the time between gas kinetic collisions, and consequently has a pure radiative character. Collisionless (instantaneous) dissociation is characterized by the presence of an intensity threshold (10^8-10^9 W/cm^2), and also by a threshold for the total transmitted energy and the time delay between the maximum of the field and the maximum degree of dissociation. Instantaneous dissociation was used to initiate an isotopically-selective reaction of the molecules of BCl_3 with gas. [5] Nonetheless, the mechanism of instantaneous dissociation has not yet been fully clarified. The mechanism of radiative dissociation due to multiphoton processes in nonresonant laser radiation was considered in [6]. However, although the estimates of the power flux density obtained in [6] coincide with those observed in experiments, on the whole this description does not agree with the observed behavior.

We analyze a possible mechanism of excitation of high vibrational levels of molecules under the influence of high-power pulsed resonant field of a laser, based on a stepwise accumulation of energy a sequence of quasi-continuous energy levels of the molecule.

It is known that in diatomic molecules, owing to the anharmonicity of the vibrations, the radiation that is resonant for the first vibrational level is not resonant for the higher vibrational levels. In the case of polyatomic molecules, the deviation of the radiation from resonance following excitation of the higher vibrational levels can in principle be compensated by the presence of a large level density. This circumstance was pointed out in [3], where it was proposed that vibrational energy can be accumulated in a quasi-continuous sequence of higher vibrational levels.

The total number of vibrational levels (including combination levels) corresponding to excitation of s vibrational quanta in l vibration modes is given by the binomial coefficient C_{s+l+1}^{s}. This number first increases rapidly with increasing s, i.e., with increasing vibrational excitation of the molecule upward on the energy scale. At $l \sim s$ the growth slows down. To each vibrational level there corresponds a rotational structure, which also contains a large number of levels. In the case of the BCl_3 molecule, in which there are two nondegenerate and two doubly degenerate vibrations ($l = 6$) and the rotational states of the symmetrical top are $B_1 = 0.1$ cm^{-1}, and $B_2 = 0.05$ cm^{-1}, the distance between the rotational sublevels, with allowance for the Coriolis splitting for the excitation energies corresponding to the absorption of one or two laser-radiation quanta ($(1-2)h\nu_3$), is $10^{-2}-5\times10^{-2}$ cm^{-1}. Thus, for the lower vibrational levels, the distance between the rotational sublevels is still large enough. At the same time, for energies on the order of $(3-4)h\nu_3$, in view of the increase of the level density, the average distance between them decreases and becomes commensurate with the homogeneous width of the rotational level (10^{-3} cm^{-1}) at pressures on the order of several torr and at room temperature.

The excitation of the first vibrational levels is possible for nonresonant absorption in a strong field, leading to "broadening" of the levels. A similar mechanism was considered in [7] for a diatomic molecule and in [8] for an N-level anharmonic oscillator. For the excitation of higher vibrational levels close to the dissociation limit, this mechanism calls for exceedingly high intensities, by virtue of the detuning that builds up with increasing number of the level. After overcoming several (two or three) first vibrational levels, the absorption becomes resonant by virtue of the increased level density, and this leads in final analysis to instantaneous dissociation. It should be noted that transitions resonant with the field are (generally speaking) forbidden in the adiabatic approximation. One can expect the dipole moment of such transitions to be smaller by one or two orders than the dipole moment of an allowed transition.

Thus, the analysis will be carried out within the

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framework of the following model: The molecule is represented by a system of N energy levels with a certain arbitrary irregular variation of the dipole moment over the levels. The frequencies of several of the lower transitions deviate from the laser-field frequency, while the remaining transitions are at resonance with the radiation.

To find the conditions of the effective radiative population of the upper levels, we consider the evolution of the density matrix ρ of an N-level system under the influence of a laser field. From the equation of motion of the density matrix

$$i\hbar\dot{\rho}=[\hat{H},\rho],\quad \hat{H}=\hat{H}_0+\hat{H}_{int} \tag{1}$$

with initial condition

$$\rho(-\infty)=\exp\{-\hat{H}_0/kT\}$$

we get for the S-matrix of the transition from the interaction representation to the Heisenberg representation, in the interaction representation, the equation

$$i\hbar\dot{S}=\hat{H}_{int}S, \tag{2}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian, $\hat{H}_{int}$ is the Hamiltonian of the interaction of the molecule with the field **E**. For a field $\mathbf{E} = \mathbf{e}\mathscr{E}(t)\cos(\omega t+\varphi)$ we have

$$\hat{H}_{mn}^{int}=\mathscr{E}(t)[(\mathbf{e}d_{mn}{}^{+})\exp\{i(\Delta\omega_{mn}t+\varphi)\}+\text{c.c.}], \tag{3}$$

where $\Delta\omega_{mn} = \omega_{mn}-\omega$ is the detuning between the frequencies of the transition fields, due for example to anharmonicity; d^+ and $d^{+*}\equiv d^-$ are respectively the components of the dipole moment operator above and below the diagonal; m and n number the energy levels.

The solution of (2) is written in the form

$$S=T\exp\left\{-\frac{i}{\hbar}\int_{-\infty}^{t}\hat{H}_{int}\,dt\right\}, \tag{4}$$

where T is the chronological-ordering operator.

The determination of the S matrix from formula (4) is in general quite difficult. It makes sense, however, to consider two limiting cases that yield the characteristic parameters of the effective passage of the lower detuned levels (I) and the population of the upper resonant levels (II).

I. The detunings are large $\Delta\omega \gg 1/\tau$ (τ is the pulse duration). In this case the integral in (4) is transformed into

$$\int_{-\infty}^{t}\hat{H}_{int}\,dt=\mathscr{E}(t)\left[\frac{\mathbf{e}d_{mn}{}^{+}}{\Delta\omega_{mn}}\exp\{i(\Delta\omega_{mn}t+\varphi)\}+\text{c.c.}\right]. \tag{5}$$

In the random-phase approximation this operator commutes with itself at any instant of time, therefore in (4) the T-ordering symbol can be left out.

$$S=\exp\left\{\frac{-i\mathscr{E}(t)}{\hbar}\left[\frac{\mathbf{e}d^{+}}{\Delta\omega}\exp\{i(\Delta\omega t+\varphi)\}+\text{c.c.}\right]\right\}. \tag{6}$$

The diagonal terms of the density matrix take the form

$$\rho_{nn}\infty\sum_{q}S_{nq}S_{qn}{}^{-1}, \tag{7}$$

where q is the rotational sublevel of the vibrational ground level (we assume that in the absence of the field only the ground vibrational level is populated). We expand the right-hand side in a series and take $\langle n|$ and $|q\rangle$ in the brackets; the first nonzero term in the expansion then the one containing $(d^+)^n$ or, in other words, proportional to $\mathscr{E}^{2n}$. We obtain

$$\rho_{nn}\infty\sum_{q}\left\langle n\left|\left(\frac{\mathbf{d}^{+}}{\Delta\omega}\mathbf{e}\right)^{n}\right|q\right\rangle\left\langle q\left|\left(\frac{\mathbf{d}^{-}}{\Delta\omega}\mathbf{e}\right)^{n}\right|n\right\rangle\frac{\mathscr{E}^{2n}}{\hbar^{2n}}+\ldots$$

It follows therefore that ρ_{nn} increases strongly when a certain threshold laser-radiation intensity is reached.

$$I_{\text{thr}}\approx\frac{c\hbar^2}{4\pi}\left[\sum_{q}\left\langle n\left|\left(\frac{\mathbf{d}^{+}}{\Delta\omega}\mathbf{e}\right)^{n}\right|q\right\rangle\left\langle q\left|\left(\frac{\mathbf{d}^{-}}{\Delta\omega}\mathbf{e}\right)^{n}\right|n\right\rangle\right]^{-1/n}. \tag{8}$$

Thus, it follows directly from (6) and (7) that upon excitation of the vibrational levels whose energies is equal to the energy of n quanta of laser radiation the excitation efficiency is proportional to I^n, the effect has essentially a threshold character, and the threshold intensity is given by formula (8).

II. The detunings are small, $\Delta\omega \ll 1/\tau$. In this case the integral (4) takes the form

$$\int_{-\infty}^{t}\hat{H}_{int}\,dt=(\hat{\mathbf{d}}\mathbf{e})\int_{-\infty}^{t}\mathscr{E}(t)\,dt \tag{9}$$

and consequently

$$S_{mn}=\exp\left\{-\frac{i}{\hbar}(\hat{\mathbf{d}}\mathbf{e})\int_{-\infty}^{t}\mathscr{E}(t)\,dt\right\}_{mn}. \tag{10}$$

Formula (10) is analogous to the expression that arises in the analysis of coherent effects of the photon-echo type in the two-level system. The main difference lies in the fact that the molecules proceed upwards under the influence of the radiation rate that is fast in comparison with the relaxation rate. It is therefore possible, at sufficiently high intensities, to neglect the relaxation of the off-diagonal matrix elements ρ_{mn}. As will be seen from the estimates below for τ_{min}, the relaxation in BCl_3 (T_2 = 27 nsec/Torr [9]) can be neglected up to pressures on the order of several torr.

We expand expression (10) in a series similar to that of (6):

$$\rho_{nn}\infty\sum_{q}\langle n|(\hat{\mathbf{d}}\mathbf{e})^{n}|q\rangle\langle q|(\hat{\mathbf{d}}\mathbf{e})^{n}|n\rangle\frac{1}{\hbar}\int_{-\infty}\mathscr{E}(t)\,dt+\ldots \tag{11}$$

It is clear therefore that for excitation of the higher vibration levels an important role is assumed by the threshold of the integral of the envelope of the pulse, and not by the intensity threshold.

$$\int_{-\infty}^{+\infty}\mathscr{E}(t)\,dt\sim\hbar/d_{\text{forb}}. \tag{12}$$

At a given value of the intensity, this condition imposes essentially a limitation on the minimum duration of the exciting pulse.

Thus, the foregoing analysis shows that actually, in the case of polyatomic molecules, the excitation of the higher vibrational levels, up to dissociation, is possible by a pure radiative mechanism, which takes into account both the level broadening under the influence of the strong field and in the presence of a high-energy density of the molecule. In a real situation, the excitation channel that is realized is a certain synthesis of the considered limiting cases of large and small detunings between the field frequency and the transition frequency and, upon excitation of several low-lying vibrational levels, the first limit in case of large detunings but allowed transitions is realized; this imposes a limitation on the intensity of the exciting pulses. Upon population of higher vibrational states, up to the dissociation limit, the second limiting case of forbidden resonant transitions is realized, and this imposes a limitation on the minimum duration of the exciting pulses.

Let us estimate the threshold value of the intensity of excitation of the first two or three vibrational levels, starting from the relation (8):

$$I_{\text{thr}} \approx \frac{c}{4\pi}\left(\frac{\hbar\Delta\omega}{d}\right)^2.$$

For the concrete case of the BCl_3 molecule, which has a vibrational-transition dipole moment $d \approx 3 \times 10^{-19}$ cgs esu[9] and anharmonicity $\Delta\omega \sim 3\ \text{cm}^{-1}$, the value of the threshold intensity amounts to 10^8 W/cm^2 and agrees with the known experimental data.[3,4]

The presence of the process of population of a quasi-continuous sequence of upper levels in the excitation cascade causes the degree of dissociation to be dependent on the pulse duration. As already noted, forbidden transitions occur in the second limiting case. The values of the dipole moments of the forbidden transitions, calculated in the nonadiabatic approximation for the HD molecule[10], were close for all the rotational-forbidden lines $d_{\text{forb}} \approx d\sqrt{m_e/M}$, where m_e is the electron mass, M is the reduced mass of the nuclei, d is the dipole moment of the allowed vibrational transition. Since the quantities d_{forb} are caused by violation of the symmetry of the limiting Ψ functions, this constitutes a lower bound for polyatomic molecules having a lower degree of symmetry.

An estimate of the minimum duration of the exciting pulses from relation (12), if the start from the values of the threshold intensity 10^8 W/cm^2 and forbidden-transition dipole moment $d_{\text{forb}} \approx 10^{-2}$ d, yields a value $\tau_{\min} \sim 10^{-8}$—10^{-9} sec. We note that the obtained value of $\tau_{\min}$ is lower than both the radiation-pulse duration and the time T_2.

The foregoing analysis points out the characteristic features of the radiative dissociation mechanism. First, the specific features of the molecular bond are lost here, all the levels are "the same" and constitute a single quasi-continuous background. There is no selectivity with respect to the vibration mode. Second, the bottleneck here lies in the lower vibration levels, where the distance between the rotational sublevels is largest, and therefore there is selectivity with respect to molecules under different conditions and with respect to molecules containing different isotopes. Third, radiative dissociation can be controlled not only by varying the frequency, but also by varying the power and duration of the exciting-radiation pulse.

We note that dissociation can be realized at low pressures for which the level broadening necessary for the effective realization of the second limiting case is due not to collisions but to the strong field which is present in accordance with the first limiting case of the presented analysis. At large values, an important role can be played by collision-radiative cascade processes of excitation of higher vibrational levels. They can be considered on the basis of the analysis developed in the present article and in[11].

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