

## DISSOCIATION OF MOLECULES IN A STRONG RADIATION FIELD

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The photodissociation of molecules in a strong (laser) radiation field is considered for  $\hbar\omega < D_0$ , where  $D_0$  is the dissociation energy. The mechanism of dissociation of polar diatomic molecules by strong buildup of their oscillations is analyzed in detail. The analysis is carried out by perturbation theory, and the probabilities for two- and three-photon dissociation are calculated. Numerical estimates show that the dissociation process due to this mechanism should be observable.

1. In the action of a strong radiation field on atoms and molecules, processes of photo-ionization and photo-dissociation can become extremely probable even under the conditions  $\hbar\omega < I_0$  and  $\hbar\omega < D_0$ , where  $\hbar\omega$  is the magnitude of the quantum of radiation and  $I_0$  and  $D_0$  are the energies of ionization and dissociation, respectively. The question of such a process of non-resonant photo-ionization of atoms was partially considered earlier.<sup>[1]</sup> The present paper is concerned with the study of the process of dissociation of molecules in the radiation field of a ruby laser (or generation near to it in frequency); in this case  $\hbar\omega \approx 1.78$  eV. In order to keep the theoretical analysis simple, we shall limit ourselves to a treatment of diatomic molecules.

Two mechanisms of photo-dissociation are possible. The first consists in the excitation of the molecule to an electronic term of repulsion with subsequent rapid decomposition of the molecule into atoms or ions. Until now such processes have been observed only in one-photon transitions in ultraviolet light (see, for example, <sup>[2]</sup>). Obviously, the type of molecular bond should have nothing to do with the probability of such a dissociation process.

The second dissociation mechanism, which will be considered below, on the other hand depends on whether the molecule is polar or homopolar. We have in mind a process of dissociation of the molecule by means of a strong buildup of its vibrations or, in other words, by means of excitation of high vibrational states of the molecule with transition into the continuous spectrum. For existing radiation densities such a buildup can be effective only for polar molecules that have appreciable infrared absorption spectra and is accomplished by the di-

rect interaction of the average (over the electronic state) electric dipole moment of the molecule  $\mu(r)$  ( $r$  is the internuclear spacing) with the electric field of the radiation  $\mathcal{E}_0 \cos \omega t$ . For homopolar molecules such spectra are either absent entirely (if the molecule has a center of symmetry;  $\mu(r) \equiv 0$ ), or they have extremely weak intensity (if the effective charge  $e_1 \equiv (d\mu/dr)_{r=r_e} \ll e$ , where  $e$  is the electronic charge). In what follows we shall consider only polar molecules, for which the effective charge is not too small compared to the electronic charge.<sup>1)</sup>

2. The quantitative analysis presented below pertains to a model of the molecule that takes into account only its vibrational degree of freedom. The electronic state of the molecule in the vibration process is assumed only to change adiabatically with a change in the spacing  $r$ , which is allowed for by the dependence of the energy of this state on  $r$ .

We consider the motion of a particle with reduced mass  $M = M_1 M_2 / (M_1 + M_2)$ , where  $M_1$  and  $M_2$  are the nuclear masses, under the influence of a perturbation with the operator  $-\mu(r)\mathcal{E}_0 \cos \omega t$  and in a potential field  $U_0(r)$  representing the total energy of the molecule in its ground electronic state with a given internuclear separation  $r$ . The function  $U_0(r)$  has one minimum at  $r = r_e$  (we set  $U_0(r_e) = 0$ ) and at  $(r - r_e) \rightarrow \infty$  tends asymptoti-

<sup>1)</sup>We note that the division here adopted of molecules into polar or homopolar types on the basis of the magnitude of the effective charge is not universal. This division is also made (see, for example, <sup>[3]</sup>) on the basis of the character of asymptotic behavior of the function  $\mu(r)$  as  $r \rightarrow \infty$ ; in case  $\mu(r) \rightarrow \text{const} \times r$ , one speaks of a polar bond (the molecule dissociates into ions), in case  $\mu(r) \rightarrow 0$ , one speaks of a homopolar bond (the molecule dissociates into atoms).

cally to the constant value  $D_e = D_0 + E_0$ , where  $E_0$  is the ground vibrational level of energy. Dissociation of the molecule corresponds to a transition of the particle to a state of the continuous energy spectrum which lies above the level  $D_e$ . In the states of the discrete spectrum the particle performs anharmonic vibrations. In calculations we shall approximate the function  $U_0(r)$  by the Morse potential<sup>[4,5]</sup>:

$$U(x) = D_e(1 - e^{-\alpha x})^2, \quad x = r - r_e. \quad (1)$$

The levels  $E_n$  are then determined by the formula (also obtained from second-order perturbation theory for the anharmonic oscillator)

$$E_n = \hbar\omega_e(n + 1/2) - \hbar\omega_e x_e(n + 1/2)^2, \quad n = 0, 1, \dots$$

$$\omega_e^2 = \frac{1}{M} \left( \frac{d^2 U}{dx^2} \right)_{x=0} = \frac{2\alpha^2 D_e}{M}, \quad x_e = \frac{\hbar\omega_e}{4D_e}. \quad (2)$$

For the majority of molecules the quantity  $x_e$  is of the order  $10^{-2}$ . The ratio of the frequencies  $\omega/\omega_e$  lies in the interval from several units to several tens, and thus the interaction of the molecular vibrations with the radiation field  $\mathcal{E}_0 \cos \omega t$  is possible only because of the anharmonic character of the vibrations, which allows transitions with  $|\Delta n| > 1$ . In the case of interest to us,  $\hbar\omega < D_0$ , the transition of the particle to the continuous spectrum (dissociation of the molecule) is possible only as a result of a multi-photon process. The dissociation energies  $D_0$  of the majority of diatomic molecules are in the interval 2–5 eV, i.e., they are spanned by two or three quanta  $\hbar\omega$ . In what follows we shall assume that at the initial moment (prior to exposure) the molecule is in the ground vibrational state  $n = 0$  and accordingly calculate the probabilities of two- and three-photon processes of dissociation.

The intensity of the transitions is determined by the matrix elements of the average dipole moment of the molecule

$$\mu_{nm} = \int_{-\infty}^{+\infty} \psi_n^*(x) \mu(r_e + x) \psi_m(x) dx, \quad (3)$$

where  $\psi_n(x)$  are the eigenfunctions of the one-dimensional motion of the particle in the potential well  $U(x)$ , which have the form<sup>[4,5]</sup>

$$\psi_n(x) = N_n \exp\{-\beta e^{-\alpha x}\} (2\beta e^{-\alpha x})^{\beta-n-1/2} L_n^{(2\beta-2n-1)}(2\beta e^{-\alpha x}),$$

$$N_n^{-2} = \frac{1}{\alpha} \sum_{s=0}^n \sum_{r=0}^n (-1)^{s+r} \binom{2\beta-n-1}{n-s} \binom{2\beta-n-1}{n-r}$$

$$\times n(n-1)\dots(s+1)n(n-1)\dots(r+1)$$

$$\times \Gamma(2\beta - 2n - 1 + s + r);$$

$$\beta = \sqrt{2MD_e} / \alpha \hbar. \quad (4)$$

In these equations  $L_n^{(p)}(x)$  is a generalized Laguerre polynomial, and  $\Gamma(x)$  is the gamma function.

Substitution of (4) in (3) leads to an integral which is easily calculated by the saddle-point method. For this we separate the factor  $\exp[-2\beta(e^{-\alpha x} + \alpha x)]$  from the integrand and observe that the parameter  $\beta$  is always of order  $10^2$ . Then the remaining part of the integrand for not too great values of the sum  $(n+m)$  (not exceeding, for example, twenty) is a slowly-varying function. Leaving only the first non-vanishing term of the expansion in powers of  $1/\beta$  arising in the saddle-point method (see, for example,<sup>[6]</sup>), we obtain<sup>2)</sup>

$$\begin{aligned} \mu_{nm} = & N_n N_m e_1 \frac{\sqrt{\pi/2}}{\alpha^2} (2\beta)^{2\beta-1/2-n-m} e^{-2\beta} \\ & \times \left\{ \left[ 2(n+m) + 3 + \frac{\mu''}{\alpha e_1} \right] L_n^{(2\beta-2n-1)} L_m^{(2\beta-2m-1)} \right. \\ & \left. + 4\beta [n L_{n-1}^{(2\beta-2n)} L_m^{(2\beta-2m-1)} + m L_n^{(2\beta-2n-1)} L_{m-1}^{(2\beta-2m)}] \right\}. \quad (5) \end{aligned}$$

In this equation the value of the argument of the Laguerre polynomial equals  $(2\beta)$ ; the polynomial with negative lower index should be considered to be identically equal to zero. From Eq. (5), in particular, it is seen that if the condition

$$(|\mu''(r_e)| / \alpha e_1) \ll 2(n+m)$$

is fulfilled, then the intensity of the transition  $n \rightarrow m$  depends weakly on the curvature of the function  $\mu(r)$  and consequently also on its asymptotic behavior for large  $r$  (see first footnote). We assume that this condition is fulfilled and accordingly do not take account of the contribution from the term  $\sim \mu''$ . A numerical calculation from Eq. (5), for example, of the matrix elements  $\mu_{5,0}$  and  $\mu_{10,5}$  with  $e_1 \sim e$  and  $\alpha \sim 10^8 \text{ cm}^{-1}$  gives  $3.8 \times 10^{-3}$  and  $2 \times 10^{-3} \text{ D}$ .

For transition from the discrete spectrum to the continuous one with energy  $E = E_n + \hbar\omega > D_e$  it is necessary to understand by the function  $\psi_m(x)$  in (3) the corresponding function of the continuum  $\psi_E(x)$ . As is well known, we may with high accuracy use a semiclassical approximation for this function, i.e., a plane wave with variable momentum  $p(x) = [2M(E - U(x))]^{1/2}$ . For our purposes, however, the form of the function  $\psi_E(x)$  can be simplified still further by considering that the principal contribution to the integral (3) is due to the neighborhood of points  $x$  that satisfy the condition  $U(x) = E_n = E - \hbar\omega$  (in this neighborhood

<sup>2)</sup>In calculating the integral (3), the function  $\mu(r_e + x)$  was expanded in powers of  $x$ ;  $e_1 = (d\mu/dr)_{r=r_e}$ ;  $\mu'' = (d^2\mu/dr^2)_{r=r_e}$ .

the function of the discrete spectrum  $\psi_n(x)$  has maximum oscillation amplitudes). Namely, the momentum in the plane wave  $\psi_E(x)$  can be considered as constant and equal to  $p_1 = [2M(E - E_n)]^{1/2} = (2M\hbar\omega)^{1/2}$ , i.e., we can place  $\psi_E(x) = L^{-1/2} \exp(ip_1x/\hbar)$  ( $L$  is an arbitrary length; normalization to unity is assumed). For the calculation of the integral (3) for a transition to the continuous spectrum it is also perfectly permissible for our estimates to take, in place of the function  $\psi_n(x)$ , the corresponding function of the linear oscillator

$$\psi_n^{(0)}(x) = C_n e^{-x^2/2\sigma^2} H_n(x/\sigma), \quad (6)$$

where  $H_n(\xi)$  is an Hermite polynomial,  $\sigma^2 = \hbar/M\omega_e$ . Then we obtain

$$\begin{aligned} \mu_{nE} &= e_1 L^{-1/2} \bar{x}_{nE}, \\ \bar{x}_{nE} &= C_n \int_{-\infty}^{\infty} e^{-x^2/2\sigma^2} H_n(x/\sigma) e^{ip_1x/\hbar} x dx \\ &= \pi^{1/4} \left( \frac{\hbar}{M\omega_e} \right)^{3/4} \frac{e^{-\omega/\omega_e}}{\sqrt{2^{n-1}(n-1)!}} \left[ V \bar{n} H_{n-1} \left( \sqrt{\frac{2\omega}{\omega_e}} \right) \right. \\ &\quad \left. + \frac{1}{2} \sqrt{\frac{2\omega}{\omega_e}} H_{n+1} \left( \sqrt{\frac{2\omega}{\omega_e}} \right) \right]. \end{aligned} \quad (7)$$

We observe that the quantity  $\bar{x}_{nE}$  has the dimensions of (length) $^{3/2}$ . Numerical calculation from this formula for  $n = 5$  ( $\omega/\omega_e \approx 5$ ),  $M \approx 10^{-23}$  g gives  $(\bar{x}_{5,E})^2 \approx 5 \times 10^{-28}$  cm $^3$ .

3. The probability of the dissociation process will depend essentially on whether or not there is a resonant transition in the discrete vibration spectrum (2). In the case of a two-photon process it is a question only of the resonance of the first transition. The transition should be considered resonant if in the spectrum (2) there is a level  $n$  satisfying the condition

$$(\omega - \omega_{n,0})^2 \ll (\mu_{n,0} \mathcal{E}_0 / \hbar)^2, \quad \omega_{n,0} = (E_n - E_0) / \hbar. \quad (8)$$

When this condition is fulfilled the probability of finding a particle in the state  $n$  must be considered different from zero even in the zeroth approximation of the perturbation ( $-\mu \mathcal{E}_0 \cos \omega t$ ) and oscillating as  $\sin^2(\mu_{n,0} \mathcal{E}_0 / 2\hbar)t$  between zero and one.<sup>[5]</sup> It follows immediately from this that the probability of two-photon dissociation  $W_{\text{res}}^{(2)}$  in this case is determined to within a factor of order unity by the transition probability  $W_{n \rightarrow E}$  under the influence of the perturbation ( $-\mu E_0 \cos \omega t$ ) from state  $n$  of the discrete spectrum to state  $E$  of the continuous spectrum; the latter is expressed by the well-known formula<sup>[5]</sup>

$$\begin{aligned} W_{n \rightarrow E} &= 2\pi \hbar^{-1} |F_{nE}|^2 \rho(p_1^2 / 2M) \\ &= 2\pi \hbar^{-1} |1/2 \mu_{nE} \mathcal{E}_0|^2 \rho(\hbar\omega), \end{aligned} \quad (9)$$

where  $\rho(E)$  is the density of states of the free one-dimensional motion of the particles, equal to  $(L/2\pi\hbar)(M/2E)^{1/2}$ . Substituting  $\rho(E)$  in Eq. (9) and using (7), we obtain

$$W_{n \rightarrow E} = (M/2\hbar\omega)^{1/2} (e_1 \bar{x}_{nE} \mathcal{E}_0 / 2\hbar)^2. \quad (10)$$

Obviously, when  $W_{n \rightarrow E} \gg \mu_{n,0} \mathcal{E}_0 / \hbar$  the probability  $W_{\text{res}}^{(2)}$  precisely equals  $W_{n \rightarrow E}$ . In the opposite case,  $W_{n \rightarrow E} \ll \mu_{n,0} \mathcal{E}_0 / \hbar$ , the total probability that the particle stays in level  $n$  equals  $1/2$  and therefore  $W_{\text{res}}^{(2)} = 1/2 W_{n \rightarrow E}$ .

For  $(\bar{x}_{nE})^2 \approx 10^{-28}$  cm $^3$ ,  $M \approx 10^{-23}$  g,  $\mathcal{E}_0 \approx 3 \times 10^7$  V/cm (this corresponds to a laser power of  $P \approx 200$  MW focused on a spot 0.1 mm in diameter),  $e_1 \sim e$ , Eq. (10) gives  $W_{\text{res}}^{(2)} \approx 5 \times 10^{10}$  sec $^{-1}$ . For  $\mathcal{E}_0 \approx 3 \times 10^6$  V/cm ( $P \approx 2$  MW) we have  $W_{\text{res}}^{(2)} \approx 5 \times 10^8$  sec $^{-1}$ .

If the resonance condition (8) is not fulfilled, then the amplitude of the probability of the particle staying in the excited state  $n$  is different from zero only in the first approximation of perturbation theory and equals<sup>[5]</sup>

$$a_n^{(1)} = \frac{\mu_{n,0} \mathcal{E}_0}{2\hbar} \frac{1 - \exp\{-i(\omega - \omega_{n,0})t\}}{\omega - \omega_{n,0}}; \quad (11)$$

then there occurs excitation of the entire series of states  $n$  with a larger probability, the larger the ratio  $\mu_{n,0}/|\omega - \omega_{n,0}|$ . For simplicity, we shall consider only one dissociation path, by fixing on a specific value of  $n$  corresponding to the maximum value of  $\mu_{n,0}/|\omega - \omega_{n,0}|$ . In this way we obtain a lower bound for the dissociation probability.

Substitution of Eq. (11) into the equation giving the amplitude of the probability  $a_E^{(2)}(t)$  of the period of the particle in a state of the continuous spectrum with energy  $E$  gives, in second-order perturbation theory (see<sup>[5]</sup>)

$$\begin{aligned} a_E^{(2)}(t) &= \frac{1}{\hbar^2} \frac{\mathcal{E}_0^2}{4} \mu_{nE} \mu_{n,0} \left[ \frac{\exp\{i(\omega_{En} + \omega_{n,0} - 2\omega)t\}}{i(\omega - \omega_{n,0})} \right. \\ &\quad \left. - \frac{\exp\{i(\omega_{En} - \omega)t\}}{i(\omega - \omega_{n,0})} \right]. \end{aligned}$$

Solving this equation for the condition  $a_E^{(2)}(0) = 0$ , forming the square of the modulus  $|a_E^{(2)}(t)|^2$ , and integrating as always over the states of the continuous spectrum that satisfy the energy conservation law  $E = E_n + \hbar\omega$ , we obtain for the dissociation probability per unit time

$$W_{\text{nonres}}^{(2)} = \sqrt{\frac{M}{8\hbar\omega}} \left( \frac{e_1 \bar{x}_{nE} \mathcal{E}_0}{2\hbar} \right)^2 \left( \frac{\mu_{n,0} \mathcal{E}_0}{\hbar \Delta\omega_1} \right)^2. \quad (12)$$

The quantity  $\Delta\omega_1 = |\omega - \omega_{n,0}|$  obviously does not exceed  $\omega_{n+1,n}/2$ . For  $\mu_{n,0} \sim 10^{-3}$  D,  $\Delta\omega_1/2\pi \approx 10^{13}$  cps, and power  $P \approx 200$  MW, the factor

$$(\mu_{n,0} \mathcal{E}_0 / \hbar \Delta\omega_1)^2 \approx 2 \cdot 10^{-4} \quad (13)$$

and the probability  $W_{\text{nonres}}^{(2)} \approx 10^7 \text{ sec}^{-1}$ .

For a power  $P \approx 2\text{MW}$  the probability  $W_{\text{nonres}}^{(2)} \approx 10^3 \text{ sec}^{-1}$ .

The equations determining  $W^{(3)}$  for the three-photon process of dissociation are obtained in analogous fashion. In this case, when both transitions in the discrete spectrum are resonant (i.e., condition (8) and one analogous to it for transition from state  $n$  to state  $m$  are fulfilled), the dissociation probability is determined in the same way<sup>3)</sup> from the probability  $W_{n \rightarrow E}$  (Eq. (10)) as is  $W_{\text{res}}^{(2)}$ . If only one transition (e.g., the second, from  $n$  to  $m$ )<sup>4)</sup> is resonant, then, as calculation shows, the probability  $W^{(3)}$  is determined by Eq. (12) with a factor  $1/2$ .

In this case, when both transitions in the discrete spectrum ( $0 \rightarrow n \rightarrow m$ ) are nonresonant, the usual solution of the equations of successive approximations for the amplitudes  $a_n(t)$  and  $a_E(t)$  leads to the following result (again an upper esti-

mate in the sense indicated above):

$$W_{\text{nonres}}^{(3)} = \frac{5}{16} \left( \frac{M}{8\hbar\omega} \right)^{1/2} \left( \frac{e_1 \bar{x}_{nE} \mathcal{E}_0}{2\hbar} \right)^2 \left( \frac{\mu_{n,0} \mathcal{E}_0}{\hbar\Delta\omega_1} \right)^2 \left( \frac{\mu_{nm} \mathcal{E}_0}{\hbar\Delta\omega_2} \right)^2, \quad (14)$$

$$\Delta\omega_2 \equiv |\omega - \omega_{mn}|.$$

We can see from this that the process of nonresonant three-photon dissociation has a low probability for the values of the field  $E_0$  considered above. However, since  $W_{\text{nonres}}^{(3)} \sim \mathcal{E}_0^6$ , then in a field  $\mathcal{E}_0 \approx 3 \times 10^8 \text{ V/cm}$  (such as will exist, for example, in focusing a power  $P \approx 200 \text{ MW}$  on a spot  $0.01 \text{ mm}$  in diameter), the probability  $W_{\text{nonres}}^{(3)} \approx 10^9 \text{ sec}^{-1}$ .

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<sup>3</sup> Vol'kenshtein, El'yashevich, and Stepanov, Kolebaniya molekul (Molecular Vibrations) **2**, Gostekhizdat, 1949.

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<sup>6</sup> L. M. Brekhovskikh, Volny v sloistyykh sredakh (Waves in Layered Media), AN SSSR, 1957. (Engl. Transl., Academic Press, N. Y., 1960).

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<sup>3)</sup>This is valid generally for an  $n$ -photon process if all transitions in the discrete spectrum are resonant.

<sup>4)</sup>Incidentally, since with increasing  $n$  the energy levels condense, while the matrix elements  $\mu_{n,m}$  for given  $|n-m|$  do not decrease, the condition (8) becomes more easily fulfilled with increasing  $n$ .