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Role of resonances associated with multiphoton transitions in molecules under the influence of an intense light field

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It is shown that electronic resonances, at internuclear distances that differ from the equilibrium value, may play an important role in multiphoton transitions in molecules. In particular, such resonances lead to a delay of the multiphoton dissociation process and to a substantial change in the angular distribution of the spreading fragments.

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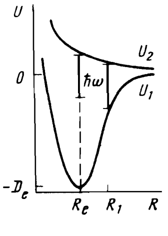
The behavior of molecules in an intense electromagnetic field has been investigated in less detail than the behavior of atoms. In particular, the specific role which electronic resonances may play in connection with multiphoton transitions in molecules has still not been analyzed. The point is that, in addition to resonances in intermediate electronic states similar to those which occur in atoms, resonances associated with different values of the internuclear distance R, differing from the equilibrium value R_e, are also possible in the system of a molecule's electronic terms. Certain effects associated with multiphoton transitions in molecules, which may be caused by resonances of a similar type, are discussed in the present article.

For the sake of definiteness let us consider the nonresonant n-photon dissociation of a diatomic molecule under the influence of an intense field of optical frequency ω. The terms of the initial U_1 and final U_2 electronic states for this case are shown schematically in the figure. After a transition to the repulsive term U_2, dissociation of the molecule usually occurs in a time of the order of 10^{-13} to 10^{-14} sec; however, this process may be significantly retarded if one-photon optical transitions between terms 1 and 2 are forbidden. For a sufficiently high intensity of radiation, the one-photon resonance $\hbar\omega = U_2(R) - U_1(R)$, appearing in the region $R_1 > R_e$, leads to a strong interaction between terms 1 and 2, as a result of which a radical rearrangement of the nuclear motion occurs. It is now necessary to determine the motion of the nuclei on the basis of the electronic Hamiltonian, which includes the resonance interaction with the radiation field.[1]

The procedure for separating the electronic and nuclear motion in a molecule located in a strong field is actually equivalent to the use of the Born–Oppenheimer approximation in the representation of "rotating" electronic states, where the resonance interaction of the molecule with the external field $\mathbf{E} = \mathbf{E}_0 \cos\omega t$ becomes time independent, and the potential energy for the nuclear motion in terms 1 and 2 takes the following matrix form:

$$\hat{U} = \begin{pmatrix} U_2 - \hbar\omega/2 & V_0 \\ V_0 & U_1 + \hbar\omega/2 \end{pmatrix}. \qquad (1)$$

The presence of the nondiagonal elements $V_0 = \mathbf{d}_{12} \cdot \mathbf{E}_0/2$ in Eq. (1) indicates that is is impossible to regard the motion of the nuclei with respect to the terms 1 and 2 as independent in the region $R \approx R_1$. Upon ful-



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fillment of the condition $(n-1)\hbar\omega < D_e$ after an n-photon transition from the ground state to term 2, with respect to its nuclear motion the molecule is found in the adiabatic potential well $U = (1/2)\{U_1 + U_2 + [(U_2 - U_1 - \hbar\omega)^2 + 4V_0^2]^{1/2}\}$, which is formed as a result of the quasi-intersection of terms 1 and 2, which are bound to each other by the interaction V_0.

One can estimate the parameters of the vibrational spectrum in this well for a fixed orientation of the molecule, assuming for simplicity constancy of V_0 and of the slopes $F_i = \partial U_i/\partial R$ of the terms in the region of the quasi-intersection:

$$\begin{gathered}\varepsilon_k = U_0 + (2k+1)\hbar\Omega/2 - (2k+1)^2\hbar\Omega x_e/4, \\ \Omega = F_1\gamma^{1/4}[(1+\gamma)MV_0/2]^{-1/2}, \\ \Omega x_e = (3/16)\hbar F_1^2\gamma M^{-1}V_0^{-2}, \\ U_0 = [b_2 + \gamma b_1 + 2V_0\gamma^{1/2} - \hbar\omega(1-\gamma)/2](1+\gamma)^{-1}.\end{gathered} \tag{2}$$

where $\gamma = |F_2/F_1|$, M is the molecule's reduced mass, and the parameters $b_i = U_i(R_1) - F_iR_i$ may include a term quadratic in E_0 and due to the nonresonant part of the polarizability. In the range R of interest to us, γ is usually less than unity, but the quantity F_1 varies over wide limits for different molecules. Not overly steep slopes, $F_1 \lesssim 10^{-4}$ cgs esu are favorable for the situation under consideration; such slopes exist in many molecules (for example, the alkali-metal halides) for $|U_1(R_1)| \approx 1$ eV. If $F_1 \approx 10^{-4}$ cgs esu, $\gamma \approx 0.2$, $M \approx 30M_p$, and $V_0 \approx 0.1$ eV, then $\Omega \approx 10^{13}$ sec and $x_e \approx 0.03$.

For a fixed orientation of the molecule, the width of the level in the formed well is determined by nonadiabatic transitions in the region of quasi-intersection of the terms, and in the case of strong coupling may be estimated from the Landau–Zener formula[2,3]

$$\Gamma = \hbar\Omega e^{-\delta}/\pi, \quad \delta = 2\pi V_0^2/\hbar v_k F_1(1+\gamma) \gg 1, \tag{3}$$

where $v_k = [2(\varepsilon_k - U_0)/M]^{1/2}$ is the quasiclassical velocity of motion of the nuclei in the quasi-intersection region. Taking account of the estimates cited above, we obtain $\delta \approx 16$ for $\varepsilon_k - U_0 \approx 0.1$ eV, i.e., the molecule's lifetime in the adiabatic well may be rather large. In fact, however, the lifetime of such a predissociated molecule will be determined by other factors, foremost among which is rotation of the molecule. A variation of the angle θ between the molecule's axis and the direction of $\mathbf{E}_0$ leads to a change in the value of V_0, and for a definite value of θ, when δ decreases to $\delta \approx 1$, the molecule will no longer be contained in the adiabatic potential well. Hence it follows that in the region R_1 the one-photon resonance may play a decisive role in the formation of the angular distribution of the dissociation products, which turns out to be dependent on the radiation intensity.

The delay induced by the field of the dissociation process already begins to significantly influence the angular distribution of the spreading fragments for $\delta_{\max} = \delta_1 \approx 1$, when the maximum lifetime of the predissociated molecule becomes comparable with the period of its rotation. For $d_{12} \approx 10^{-18}$ cgs esu and the estimates utilized above, this corresponds to an intensity $I \approx 10^{12}$ W/cm^2. With increasing intensity of the radiation, the number of molecules which dissociate at an axis orientation corresponding to the maximal value $\delta_{\max} \gg \delta_1$ will decrease rapidly, and a deep dip appears in the angular distribution for $\theta = 0$, π or $\theta = \pi/2$ respectively for "parallel" ($V_0^2 \sim \cos^2\theta$) and "perpendicular" ($V_0^2 \sim \sin^2\theta$) transitions. The width of this dip is determined by the condition $\delta \geqslant \delta_1$, i.e., for parallel resonance transitions the dissociation products will be primarily emitted in a plane which is perpendicular to $\mathbf{E}_0$ in the angular band $\Delta\theta = \pi/2 \pm \cos^{-1}(\delta_1/\delta_{\max})$, and for perpendicular transitions—around the direction $\mathbf{E}_0$ in the band $\Delta\theta = \sin^{-1}(\delta_1/\delta_{\max})^{1/2}$.

In the angular range corresponding to the condition $\delta < \delta_1$, dissociation of the molecule takes place practically without delay; in this region the angular distribution is primarily determined by the initial multiphoton transition, as a result of which the molecule falls on the repulsive term. In the absence of a buildup of molecules in the predissociated state, the emergence of a dip in the angular distribution should obviously lead to an increase in the number of molecules, which are dissociating in the region separating the band of the dip and the unperturbed distribution, i.e., it should lead to the appearance of additional maxima. Such a rearrangement of the angular distribution may be observed not only in multiphoton processes, but also for the one-photon association of molecules by ultraviolet radiation, if a strong field of smaller frequency acts on them simultaneously. In this case the change of the angular distribution may be unusually sharp, since for identical polarizations of the two fields the dip falls exactly on the position of the maximum of the unperturbed distribution.

The influence of a finite lifetime of the predissociated molecule on the angular distribution of the products of the one-photon dissociation has been previously investigated in several articles (see, for example,[4,5]). The results obtained there, however, cannot be directly utilized for a description of the characteristic features mentioned here of the angular distribution because, first of all, in the present case the delay time of the dissociation turns out to be substantially anisotropic and, furthermore, it is, generally speaking, already impossible to regard the molecular rotation in a strong radiation field as free.

Within the framework of a classical description of molecular rotation, the influence of the field-induced delay of the dissociation on the angular distribution may be taken into consideration in the following way. If $W(\cos\theta)$ is the probability of dissociation per unit time for an excited molecule with a given orientation, then for a sufficiently slow (in comparison with the vibrational frequency) variation $\theta(t)$ the probability of dissociation of the molecule into the angular interval $\sin\theta_1 \times d\theta_1$ for an initial orientation θ_0 and an initial velocity $\dot\theta_0 = \omega_0\cos\gamma_0$ will be determined by the expression $P\sin\theta_1\, d\theta_1$, where

$$P(\theta_1, \theta_0, \dot\theta_0) = \int_0^\infty \delta(\cos\theta_1 - \cos\theta)\exp\left[-\int_0^t W(t')\,dt'\right] W\,dt. \tag{4}$$

In virtue of the axial symmetry of the problem, the quantity P does not depend on the azimuthal angle. The final result is obtained after averaging the distribution (4) over the initial values θ_0 and $\dot{\theta}_0$, which are determined by the multiphoton transition of the molecule into term 2 in the presence of a strong radiation field. The calculation of the initial distribution is an independent problem and falls outside the limits of the present work. At the same time those characteristic features of the angular distribution, which were considered above, are already evident from Eq. (4). If $W/\omega_0 \ll 1$, then P turns out to be a small quantity, which corresponds to the region of the dip in the angular distribution. For $\omega_0/W \ll 1$ the values of P turn out to be localized near θ_0, that is, $P \sim \delta(\cos\theta_1 - \cos\theta_0)$, and the initial angular distribution remains practically unchanged.

If it is assumed that the molecule's rotation is free, i.e.,

$$\cos\theta = \cos\theta_0 \cos\omega_0 t + \sin\theta_0 \sin\omega_0 t \cos\gamma_0, \tag{5}$$

and the ratio of the rotational frequency ω_0 to W is small over the entire range of angles (the case of a relatively weak field), then after averaging over γ_0 the following value is obtained from Eq. (4) for the correction Δf to the initial angular distribution $f(\cos\theta_0)$:

$$\Delta f = \frac{\omega_0^2}{2}\left\{\left[(1-y^2)\frac{f}{W^2}\right]'' + \left[2y\frac{f}{W^2} + (1-y^2)\frac{fW'}{W^3}\right]'\right\}, \tag{6}$$

where the primes denote differentiation with respect to $y = \cos\theta_0$. We note that for $W(y) \neq \mathrm{const}$ the quantity Δf does not, generally speaking, vanish identically even for an isotropic initial distribution.

It was already mentioned above that the molecule's rotation in a strong field differs from free rotation. As is evident from Eqs. (2), the resonance interaction leads to the appearance of a pushing torque resonance that rotates the axis of the molecule in the direction of decreasing V_0. It is interesting to note that, upon allowance for the nonresonant part of the polarizability, stabilization of the position of the molecule's axis with respect to $\mathbf{E}_0$ may be approached if the longitudinal and transverse polarizabilities differ noticeably, $|\chi_\parallel - \chi_\perp| \geqslant 1$ Å^3. The intensities $I \geqslant 10^{13}$ W/cm^2 required for this do not exceed by far those values which are necessary to achieve the condition $\delta \gg 1$ and which are usually utilized for an experimental investigation of multiphoton transitions. Stabilization of the molecule's axis may increase the molecule's lifetime in the adiabatic potential well and may lead to an increase in the relative role of other competing processes, for example, ionization or spontaneous radiative transition.

Thus, the resonances investigated here are able to significantly influence the nature of the multiphoton transitions in molecules. The conditions of their formation are less stringent than for resonances into intermediate electronic states for $R \approx R_e$. The rearrangement of the nuclear motion which occurs in this connection differs qualitatively from the effects considered earlier,[6,7] which may be observed in connection with the collision of atoms in a radiation field of smaller intensity and at such interatomic distances when resonant modification of the terms of the quasimolecules does not lead to the formation of a discrete spectrum instead of a continuum.

The value $I \approx 10^{12}$ W/cm^2, necessary for the manifestation of this specific role of the electronic resonances, at the same time does not exceed those values, when perturbation theory becomes inapplicable for nonresonant processes. For example, in order for one-photon dissociation from the adiabatic well to have[9] significant influence on the general picture of n-photon dissociation (this would imply an increase in the relative role of the $(n+1)$st order process), in the present case it is necessary that the cross section for one-photon dissociation exceeds the value $\sigma = \omega_0(\hbar\omega/I) \approx 10^{-19}$ cm^2, whereas the cross section for such processes is usually considerably smaller, owing to nonobservance of the Franck–Condon principle. If the influence of such a transition nevertheless becomes appreciable (in connection with a further increase of the intensity or in the presence of a close, repulsive term U_3), then fragments having different energies with respect to the motion or existing in different electronic states appear among the dissociation products. This example is obviously one more illustration of the effect considered in the present work, which consists of an increase in the relative role of processes which compete with n-photon dissociation through term 2, when the latter turns out to be suppressed by the anisotropic adiabatic barrier which arises as a consequence of the strong resonant interaction between terms 1 and 2. Resonances of this type can modify the nuclear motion not only in the initial and final states, but also in any other electronic states between which a resonant interaction arises. This circumstance leads, in particular, to additional restrictions on the validity of the usual Born–Oppenheimer approximation, and these additional restrictions must be taken into account upon consideration of multiphoton transitions in molecules which are located in an intense light field.

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