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STRONG EXCITATION AND DISSOCIATION OF MOLECULES IN AN INTENSE LIGHT FIELD

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Excitation of vibrational oscillations of molecules and their dissociation in an intense light field are considered. The probabilities for these processes, calculated on the basis of the one-dimensional Morse oscillator model of the molecule are given. Various excitation channels are considered, such as resonance at the fundamental vibrational frequency (modulated light field), direct transfer across several levels, and absorption of quanta at the fundamental, doubled, or hybrid frequency. The possibility is investigated of using the force due to polarization of atoms in molecules in a light field to build-up the oscillations.

1. INTRODUCTION

THE availability of powerful sources of coherent light uncovers new possibilities of acting on molecular and intermolecular processes, such as excitation and dissociation of molecules, change in the interaction between atoms, change in the structures of molecules, initiation and acceleration of chemical reactions, molecular heating of matter, etc.

In this article we consider the probabilities of excitation and dissociation of molecules in a coherent light field. This question was previously dealt with in two articles [1,2]. The author has shown in [1] the possibility and the conditions for a rapid strong resonant excitation of homopolar and heteropolar molecules, and has demonstrated that the polarization of the atoms and molecules leads to the appearance of forces that depend on the square of the field intensity and that pulsate with a frequency equal to double the frequency of light or to double the frequency of modulation of the light by mixing of close frequencies. Satisfaction of special conditions is necessary for fundamental resonant oscillations to build up, because the light frequency of the employed powerful generators is several times larger than the natural vibrational frequency, but the quantum energy is insufficient for direct dissociation of the molecule.

The paper of Bunkin et al.[2] was devoted to a calculation of the probabilities of two- and three-quantum dissociations of heteropolar molecules with resonant absorption of quanta, exceeding by several times the distances between the levels (the probabilities of such transitions are very small in the equidistant region of levels, and become noticeable only when the nonlinearity is noticeable). In practice, however, it is difficult to use the results of this article, because the calculations are only half-finished, no final expressions are obtained for the matrix elements of the dipole transitions, and the obtained expressions for the probabilities of the transition to the continuous spectrum are too approximate (the wave functions used were those of a harmonic oscillator for the bound state and of an unperturbed plane wave for the continuous spectrum, which is an incorrect procedure at the low prevailing scattering energies, smaller than or comparable with the dissociation energy). These approximations are not justified, since all these expressions can be accurately calculated for a Morse oscillator.

We note also that the use of the Morse oscillator to describe heteropolar molecules [2] is not always valid, since this oscillator is usually employed to describe homopolar molecules, which interest us most. However, the deductions obtained will be typical for any potential curve which describes more or less correctly vibrations of atoms in a molecule.

Thus, we consider first transitions induced by a force, with amplitude f_0 and frequency ω_f, acting on a Morse oscillator. The values of f_0 and ω_f are determined by the field of the light wave and by the type of the molecule in accordance with the relations of Sec. 4.

2. EXCITATION OF MORSE OSCILLATOR

It is known that a Morse oscillator [3] with potential

$$U(x) = D\{e^{-\alpha x} - 2e^{-2\alpha x}\}, \qquad x = X - X_e,$$

describes satisfactorily the properties of molecules in the entire vibrational-energy interval. Here D is the dissociation energy, and α and X_e are experimental constants. The energy eigenvalues of such an oscillator are

$$E_n = -D\{1 - (n + 1/2)/d\}^2, \qquad n = 0, 1, 2 \ldots,$$

(where $d = (2MD)^{1/2}/\alpha\hbar$ and M is the oscillator mass), describe quite accurately the spectrum of the vibrational levels, which converges rapidly at the end of the spectrum. The eigenfunctions of the Morse oscillator are expressed in terms of generalized Laguerre polynomials and have been adequately discussed in the literature.

The matrix element of the dipole transition from the m-th to the n-th state of the Morse oscillator, induced by a force with amplitude f_0 (see, for example, [4]), is

$$F_{mn} = f_0 x_{mn} = f_0 \int \psi_m^* x \psi_n dx = f_0 \frac{\hbar^2}{M(E_m - E_n)}$$
$$\times (-1)^{m+n} \frac{\alpha}{2} \left[\frac{n!\Gamma(2d-n)}{m!\Gamma(2d-m)} (2d - 2m - 1) \right.$$
$$\left. \times (2d - 2n - 1) \right]^{1/2},$$

where Γ is the gamma function. This matrix element determines the probability of observing the system at the n-th level [5] for an almost resonant transition $E_n - E_m = \hbar(\omega_f + \epsilon)$:

$$w_n = \frac{|F_{mn}|^2}{2\hbar^2\Omega^2} (1 - \cos 2\Omega t), \qquad \Omega^2 = \left\{ \frac{\varepsilon^2}{4} + \frac{1}{\hbar^2} |F_{mn}|^2 \right\},$$

i.e., the probability is a periodic function of the time with period π/Ω varying from zero to $|F_{mn}|^2/\hbar^2\Omega^2$.

As $\epsilon \to 0$ (almost exact resonance) we have

$$w_n \to 1/2[1 - \cos(2|F_{mn}|t/\hbar)],$$

i.e., the probability varies from 0 to unity within a time $\tau \approx \pi\hbar/|F_{mn}|$. The average probability of resonant transition per unit time is $\sim 1/\tau \sim |F_{mn}|/\pi\hbar$ and is determined by the magnitude of the given matrix element.

Let us simplify the expression for the matrix element of the transition. We write

$$F_{mn} = \frac{f_0 \hbar \alpha}{2M\omega_{mn}} \varphi(m, n),$$

where

$$\varphi(m, n) = \left[\frac{n!\Gamma(2d-n)}{m!\Gamma(2d-m)} (2d - 2n - 1)(2d - 2m - 1) \right]^{1/2}$$

is a function containing the main dependence of the transition probability on the level numbers. For small excitation quantum numbers ($n, m \ll 2d \sim 10^2$), using the relation $\Gamma(A - a) = \Gamma(A)A^{-a}\exp(a^2/2A)$ with $A \gg a$, putting $A = 2d \gg 1$, and setting a equal to n or m, we obtain the simplified expression

$$\varphi(m, n) \approx \left[\frac{n! e^{(n^2-m^2)/4d}}{m!(2d)^{n-m}} \right]^{1/2} 2d \approx \left[\frac{n!}{m!(2d)^{n-m}} \right]^{1/2} 2d;$$
$$\varphi(m, n) \sim \frac{1}{(2d)^{(n-m)/2}}.$$

For example, for transitions from the normal state ($m = 0$) we obtain for $2d \approx 10^2$ the following: $\varphi(0, 1) = 10$ for $n = 1$; $\varphi(0, 2) = 1.4$ for $n = 2$; $\varphi(0, 4) = 0.05$ for $n = 4$, $\varphi(0, 10) \approx 2.3 \times 10^{-5}$ for $n = 10$, etc.

We see that the probability of a single-quantum transition decreases sufficiently rapidly with increasing number of stepped-over levels, and that in the usually realized case, when the quantum energy exceeds by an order of magnitude the energy of the vibrational quantum of first levels, it amounts to millionths of the transition probability between neighboring levels. All this emphasizes the advisability of investigating resonant passage through the equidistant region of the spectrum with the aid of a multiple successive absorption of resonant quanta (this process was considered earlier [1]).

3. DISSOCIATION OF MORSE OSCILLATOR

We now consider the dissociation of a Morse oscillator, assuming that the energy of one absorbed quantum is sufficient to bring the oscillator from an already excited or even from the ground state to the dissociated state. The probability of transition from the initial state ψ_m to the continuous spectrum with energy $E = E_m + \hbar\omega_f$ under the influence of a perturbing force with amplitude f_0 and frequency ω_f is of the form

$$w_{m \to E} = \frac{2\pi}{\hbar} |F_{mE}|^2 \rho(E),$$

where the density of the states of the free one-dimensional motion of the particle $\rho(E)$ is

$$\rho(E) = \frac{L}{2\pi\hbar} \left(\frac{M}{2E} \right)^{1/2}, \qquad F_{mE} = f_0 \int \psi_m^* x \psi_E dx.$$

We obtain this dipole matrix element of the bound-free transition directly from the expression for the matrix element of the transition F_{mn} in a manner similar to the published calculation of the matrix element corresponding not to a dipole but to an exponential interaction (such as the short-range potential in the problem of dissociation upon collision of identical particles).

The function $\Phi(E, x)$ of the continuous spectrum of the Morse oscillator is expressed in terms of the confluent hypergeometric function

$$\Phi(E,x) = \eta^{-1/2} W_{d,\, i\mu}(\eta),$$
$$\eta = 2de^{-\alpha x}, \qquad \mu = (2ME)^{1/2} / \alpha\hbar.$$

It is easy to see from the defining equation that Φ can be obtained from the non-normalized function of the discrete spectrum by making the replacement of

$$\mu_n = (-2ME_n)^{1/2} / \alpha\hbar = d - n - {}^1/_2$$

by $i\mu$, that is, $n \to d - i\mu - {}^1/_2$; thus

$$\Phi(E,x) = \{N_n \psi_n\}_{\mu_n \to i\mu},$$

where N_n is the reciprocal of the normalizing factor of the discrete-spectrum function:

$$N_n^2 = \{\Gamma(2d-n)\}^3 / \alpha(2d-2n-1)n!$$

The normalizing factor for $\Phi(E, x)$ can be determined from the fact that

$$\Phi(E,x) = \eta^{-1/2}\left\{\frac{\Gamma(-2i\mu)}{\Gamma({}^1/_2 - i\mu - d)} M_{d,\, i\mu}(\eta) + \text{c.c.}\right\},$$

where the function $\eta^{-1/2}M$ has an asymptotic form of a plane wave of unit amplitude. Therefore the normalized function of the continuous spectrum is of the form

$$\psi_E = \frac{1}{L^{1/2}} \frac{\Gamma({}^1/_2 - i\mu - d)}{\Gamma(-2i\mu)} \Phi(E,x).$$

The square of the modulus of the sought matrix element is

$$|F_{mE}|^2 = \frac{f_0^2}{L} \{|N_n\psi_n|^2\}_{\mu_n \to i\mu} \left|\frac{\Gamma({}^1/_2 - i\mu - d)}{\Gamma(-2i\mu)}\right|^2.$$

Substituting and using the relations*

$$|\Gamma(2i\mu)|^2 = \frac{\pi}{2\mu\, \text{sh}\,(2\pi\mu)},$$

$$\left|\Gamma\left(\frac{1}{2} - d - i\mu\right)\Gamma\left(\frac{1}{2} + d + i\mu\right)\right|^2 = \frac{2\pi^2}{\text{ch}\, 2\pi\mu - \cos 2\pi\mu_0}$$

where $\mu_0 = d - {}^1/_2$ and the relation

$$\left|\Gamma\left(d + \frac{1}{2} + i\mu\right)\right|^2 \approx 2\pi\, e^{-(2d+1)}\left\{\mu^2 + \left(d + \frac{1}{2}\right)^2\right\}^d$$
$$\times \exp\left\{-2\mu \,\text{arc tg}\, \frac{\mu}{d + {}^1/_2}\right\}$$

for large d, we obtain

$$|F_{mE}|^2 = \frac{f_0^2\, 2\pi^2\alpha\hbar^4(2d-2m-1)\mu\, \text{sh}\,(2\pi\mu)\, e^{-(2d+1)}\{\mu^2 + (d + {}^1/_2)^2\}^d}{LM^2(E-E_m)^2 m!\, \Gamma(2d-m)\,(\text{ch}\, 2\pi\mu - \cos 2\pi\mu_0)} \exp\left\{-2\mu \,\text{arc tg}\, \frac{\mu}{d + {}^1/_2}\right\}.$$

Since

$$\rho(E) = \frac{L}{2\pi\hbar}\left(\frac{M}{2E}\right)^{1/2} = \frac{LM}{2\pi\hbar^2\alpha\mu},$$

the transition probability per unit time is

$$w_{m\to E} = \frac{\pi\hbar(2d-2m-1)f_0^2}{M(E-E_m)^2 m!\, \Gamma(2d-m)} \varphi(\mu),$$

where

$$E - E_m = \hbar\omega_f,$$

$$\varphi(\mu) = \frac{\text{sh}\,(2\pi\mu)\, e^{-(2d+1)}[\mu^2 + (d + {}^1/_2)^2]^d}{\text{ch}\, 2\pi\mu - \cos 2\pi\mu_0}$$
$$\times \exp\left\{-2\mu \,\text{arc tg}\, \frac{\mu}{d + {}^1/_2}\right\}.$$

At low scattering energy $(2\pi\mu \ll 1)$ we have

$$\varphi(\mu) \approx \frac{2\pi\mu\, e^{-(2d+1)}(d + {}^1/_2)^{2d}}{1 + 2\pi^2\mu^2 - \cos 2\pi\mu_0} \sim \mu,$$

if μ_0 is not very close to an integer (otherwise the probability increases strongly, with $\varphi(\mu) \sim 1/\mu$). In the range $1 < \mu < \sqrt{d}$, the function varies slowly. At these and higher energies $(2\pi\mu \gg 1)$ we have

$$\varphi(\mu) \approx e^{-(2d+1)}\left\{\mu^2 + \left(d + \frac{1}{2}\right)^2\right\}^d \exp\left\{-2\mu \,\text{arc tg}\, \frac{\mu}{d + {}^1/_2}\right\}.$$

It is easy to see that $\varphi(\mu)$ has a rather sharp dip at $\mu \approx \sqrt{d}$, up to which $\varphi_{\max}(\mu) \approx \exp[-(2d+1)]\, d^{2d}$.

The main dependence of the transition probability on the number of the initial level is determined by the factor $(2d - 2m - 1)/m!\, \Gamma(2d - m)$. Since, for $m \ll 2d$,

$$\Gamma(2d - m) \approx \Gamma(2d)\,(2d)^{-m} e^{m^2/4d}$$
$$\approx (2d)^{2d - 1/2} e^{-2d}\sqrt{2\pi}\,(2d)^{-m} e^{m^2/4d},$$

we get

$$w_{m\to E} \approx \frac{(2d)^m}{m!} \frac{\hbar f_0^2}{M(E-E_m)^2} \frac{(2d)^{3/2}}{2^{2d}\sqrt{2\pi}} \sim \frac{(2d)^m}{m!}$$

that is, the dissociation probability increases with increasing number of the initial level, thus confirming the advisability of preliminary excitation of the molecule, for example, by the method de-

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*sh = sinh, ch = cosh, tg = tan, arc tg = $\tan^{-1}$.

scribed earlier[1]. At very large excitations, the tunnel disintegration of the molecule becomes noticeable, particularly in cases when f_0 depends quadratically on the light field and has a constant component.

4. POSSIBLE MODES OF EXCITATION AND DISSOCIATION OF MOLECULES BY INTENSE LIGHT WAVES

Light can act effectively on a molecule in ways that differ with regards to frequency of the exciting force and with regards to the type of the employed resonance; the resultant modes can be divided into two classes.

The first class includes cases in which the frequency of the produced exciting force coincides with the frequency of the light field: $\omega_f = \omega$, and the amplitude of the force is linear over the field. This holds for polar molecules, whose atoms have effective charges. These molecules interact strongly with the light because of the large value of the force $f_0 \approx eE_0$. Since the light frequency of the existing powerful quantum generators exceeds by 90 times the frequency of the vibrational quantum Ω_{vibr} ($\omega/\Omega_{\text{vibr}} \approx 10$), only resonant transitions across several levels are possible.

The second class includes cases when the employed exciting force has a frequency different from the optical frequencies. This can be, for example, the case when the oscillations are excited by the force resulting from the polarization change in the interaction between the atoms. As was shown earlier[1], this force is $f_0 \approx a^2E_0^2$, where a is the dimension of the atom, equivalent to a field intensity

$$E_{\text{экв}} \approx a^2E_0^2 / e \approx (a^2E_0 / e)E_0.$$

For example, at the prevailing $E_0 \approx 3 \times 10^6$—$3 \times 10^7$ V/cm, we get

$$E_{\text{eg}} / E \approx a^2E_0 / e \approx 10^{-3} - 10^{-2}.$$

Such a force can act in any molecule in which the atoms can become polarized, that is, in both homopolar and heteropolar molecules. It becomes effective when the intensity of the wave increases, and can give rise to new absorption lines only when the light intensity is high. Thus, for example for homopolar molecules, absorption lines appear in those regions of the spectrum where these molecules show no optical activity in a low-intensity light flux.

Since the force of interaction of the polarized molecules is quadratic in the field, the spectrum of the force will contain frequencies double those of the light, $\omega_f = 2\omega$, and also combination frequencies, which appear if light fluxes of different frequencies are used. For example, if light fluxes with two frequencies are mixed, the spectrum of the force

$$f(t) = (E_{10}\sin\omega_1 t + E_{20}\sin\omega_2 t)^2 = f_{10}\sin 2\omega_1 t + f_{20}\sin 2\omega_2 t$$
$$+ f_{12}\cos(\omega_1 - \omega_2)t - f_{12}\cos(\omega_1 + \omega_2)t + f_0$$

contains four frequencies: $2\omega_1$, $2\omega_2$, $\omega_1 - \omega_2$, and $\omega_1 + \omega_2$. When $\omega_1 - \omega_2 \ll \omega$, two effective frequencies remain, 2ω and $\Delta\omega = \omega_1 - \omega_2 = 2\omega_{\text{mod}}$, where ω_{mod} is the modulation frequency of the light-field amplitude. The presence of difference and hybrid frequencies broadens the range of selection of resonant conditions, making it possible to realize them even in the infrared band, where the resonant frequencies of the vibration oscillations lie. Doubling the frequency of the force also makes it possible to realize in some cases a transition to upper levels or to the continuous spectrum. The use of radiation from a nonlinear element that doubles the frequency of a high-intensity beam as the fundamental frequency makes it possible to obtain quantum energies exceeding the molecule-dissociation energies.

In the equidistant region of the spectrum, the probability of excitation of the n-th level can be estimated from the formula for the excitation of the harmonic oscillator of frequency Ω_{vib}

$$w_n = \frac{(\varepsilon/\hbar\Omega_{\text{vibr}})^n}{n!}\exp\left\{-\frac{\varepsilon}{\hbar\Omega_{\text{vibr}}}\right\},$$

where ϵ denotes the classical work performed by the external force on the oscillator. For example, in the case of exact resonance (up to the occurrence of the detuning) the growth of the amplitude $x_0(t) \approx f_0 t/2M\Omega_{\text{vibr}}$ and $\epsilon(t) \approx kx_0^2 \approx f_0^2t^2/4M$. A frequency deviation appears at $t \sim 1/\Delta\Omega$, and therefore $\epsilon_{\max}(t) \approx f_0^2/{}^4M(\Delta\Omega)^2$. Even this shows the sharp increase in the probability of excitation when resonance is approached and when the amplitude of the effective force increases.

Let us consider now some features of resonant interaction between a large-amplitude light field and a quantum system. The first singularity of the intense interaction is an increase in the limits of the permissible detuning with increasing interaction amplitude. Indeed, from the formula for the probability of nearly resonant transition[5]

$$w_n = \frac{2|F_{mn}|^2}{(\hbar^2\varepsilon^2 + 4|F_{mn}|^2)}\left\{1 - \cos\left(\varepsilon^2 + \frac{4}{\hbar^2}|F_{mn}|^2\right)^{1/2} t\right\}$$

we see that the condition of exact resonance is satisfied if the frequency detuning is

$$\varepsilon = \omega_f - \omega_{\text{res}} < \frac{4}{\hbar}|F_{mn}| = \frac{4}{\hbar}f_0|x_{mn}|.$$

Therefore, an increase in the permissible detuning takes place with increasing amplitude of the force f_0. The width of the resonance is $\Delta\omega_f/\omega_f = 2f_0\alpha\varphi_{mn}/M\omega_f^2$. For example, for polar systems, going across several levels, $\Delta\omega/\omega \approx 2eE_a\varphi_{mn}/Ma\omega^2 \sim 10^{-4}$ for $E_a \approx 3 \times 10^7$ V/cm, $M \approx 10^{-24}$ g, $\omega \approx 3 \times 10^{15}$ sec^{-1}, and $\varphi_{0,4} \approx 5 \times 10^{-2}$, but for polarizable systems and for transitions to close-lying first levels ($x_{mn} \sim a$) we obtain $\Delta\omega_f/\omega_f \approx (2aE_0^2/M\omega_f^2)\varphi_{0,1} \sim 10^{-2}$ for $\omega_f \sim \omega/5$ and $\varphi_{0,1} \approx 10$, which is much larger than the width of the laser line or the width of the modulation-frequency line.

It must be noted that the rotational motion of the molecules (which is almost always present), and the rocking of the molecules upon application of the field, lead to modulation of the effective oscillation-buildup force (rotation of the axis about which the oscillations are built up relative to the field polarization), and this also broadens the spectrum of the buildup force and facilitates the choice of resonance.

A strong light field causes also broadening and oscillation of the levels. It is most strongly manifest for molecules with dipole moments (the level shift in this case is $\Delta U \sim pE(t) \sim eaE(t)$; for homopolar molecules the shift $\Delta U \sim a^3E^2(t)$ is smaller in magnitude).

We see from the foregoing the great prospects of using different channels of strong excitation and dissociation of molecules by coherent light fluxes. Resonant buildup of oscillations is possible at frequencies which differ from the frequency of the light, and combined simultaneous resonant action at several resonant frequencies is possible. The development of techniques for converting the frequencies of coherent generators (with the aid of induced combination processes, nonlinear harmonic generators, etc.) facilitates the conditions of frequency selection.

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