Excitation of high vibrational states and dissociation of polyatomic molecules in a laser field

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The vibrational states of molecules with degenerate modes are considered. It is shown that anharmonicity leads to the removal of degeneracy and to the formation of level "bands" which may "overlap" the harmonic levels. The population kinetics for an almost resonant multilevel system is discussed. It is shown that there are two qualitatively different ways of populating the upper vibrational levels, which are designated as the tunneling and the classical mechanisms. The results obtained from this analysis are used to explain the instantaneous dissociation of polyatomic molecules. Estimates are given for the probability of dissociation of an excited molecule in a laser field.

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Theoretical analysis of the cascade population of the upper vibrational states of a molecule can be divided into two main stages. The first stage involves the determination of the spectrum of energy levels of the molecule, which are involved in the cascade process, and the second stage is concerned with the population dynamics for this energy level scheme. The spectrum of energy eigenvalues of molecules has been under investigation for a considerable time. The Morse oscillator model[1,2] has been proposed for the analysis of the population of high vibrational states. In general, this model corresponds to the diatomic molecule and, in this case, the intensity necessary for the effective population of high vibrational states is too high and exceeds, for example, the gas breakdown threshold. The quasicontinuum model was discussed in our previous paper.[3] This model corresponds to the case of polyatomic molecules, and is based on the idea that, as the vibrational quantum number increases, there is a rapid increase in the level density of polyatomic molecules, so that resonance transitions take place to high vibrational states. Much lower intensities are required by this model for reaching the high vibrational levels, and these intensities are in good agreement with experimental data.[4,5] Further analysis of the quasicontinuum model requires the inclusion of the degeneracy of vibrational modes of the molecule. Removal of this degeneracy through the inclusion of anharmonicity leads to the appearance of bands of relatively well resolved transitions on the quasicontinuum background, and this facilitates the excitation of high vibrational states of the molecule.

In this paper, we consider the excitation of molecules with degenerate vibrational modes by a strong laser field. In Sec. 1, we shall determine the energy eigenvalues for a triply degenerate mode and will show that this spectrum is localized in the neighborhood of $n\hbar\omega$ when the molecular parameters satisfy certain conditions. In Sec. 2, we shall develop a method for describing the excitation kinetics for multilevel systems and will determine the parameter values which will ensure the effective population of the upper levels. The results obtained in Sec. 2 are used in Sec. 3 to analyze the model developed in Sec. 1. Numerical estimates are reproduced, and the results are discussed.

1. Polyatomic molecules having an axis of symmetry of order greater than 2 have degenerate vibrational modes. The presence of degeneracy may substantially facilitate the purely radiative accumulation of vibrational energy in the molecule exposed to a laser field. Let us consider the energy spectrum of a triply degenerate mode by considering a molecule XY_6 with O_h symmetry. We shall confine our attention to the vibrational Hamiltonian $\hat{H}_0$ for the mode ν_3, assuming that the vibrational energy has been averaged over the other vibrational modes.

In the coordinate frame attached rigidly to the molecule, the Hamiltonian can be written in the form

$$\hat{H}_0=\frac{1}{2m}\sum_{i=x,y,z}(\hat{p}_i^2+m^2\omega^2r_i^2)+A(x^4+y^4+z^4)+B(x^2y^2+x^2z^2+y^2z^2)+C[\mathbf{r}\hat{\mathbf{p}}]^2. \tag{1}$$

This expression includes terms up to the fourth order in the potential energy. The anharmonicity of the vibrational modes is characterized by the three constants A, B, and C, and the symmetry of the molecule is taken into account. This tensorial anharmonicity removes degeneracy, and the energy levels are shifted from their "harmonic positions," forming a band of energy states. The spectrum will be calculated within the framework of perturbation theory. The zeroth approximation will be taken in the form of the harmonic oscillator wave functions

$$\Psi_0=\Psi_{v_1}(x)\Psi_{v_2}(y)\Psi_{v_3}(z).$$

The secular equation (6) must be solved to determine the first-order corrections. To do this, we shall seek the Ψ function in the form

$$\Psi=\sum_{v_1+v_2+v_3=v}(v_1!v_2!v_3!)^{-1/2}\Psi_{v_1}\Psi_{v_2}\Psi_{v_3}b_{v_1v_2v_3}.$$

For the coefficients $b_{v_1v_2v_3}$ and the correction ε to the harmonic value of the energy, we have the equation

$$\varepsilon\mathbf{b}=\hat{H}\mathbf{b}. \tag{2}$$

The matrix elements have the form

$$\langle v_1, v_2, v_3|H|v_1, v_2, v_3\rangle=\alpha(v_1^2+v_2^2+v_3^2)+\beta(v_1v_2+v_2v_3+v_3v_1),$$

$$\langle v_1-2, v_2+2, v_3|H|v_1, v_2, v_3\rangle=\langle v_1, v_2+2, v_3-2|H|v_1, v_2, v_3\rangle$$
$$=\gamma(v_2+1)(v_2+2),$$

$$\langle v_1+2, v_2-2, v_3|H|v_1, v_2, v_3\rangle=\langle v_1+2, v_2, v_3-2|H|v_1, v_2, v_3\rangle$$
$$=\gamma(v_1+1)(v_1+2),$$

$$\langle v_1-2, v_2, v_3+2|H|v_1, v_2, v_3\rangle=\langle v_1, v_2-2, v_3+2|H|v_1, v_2, v_3\rangle$$
$$=\gamma(v_3+1)(v_3+2),$$

where

$$\alpha=6A(\hbar/2m\omega)^2,\quad \beta=4B(\hbar/2m\omega)^2+2C\hbar^2,\quad \gamma=B(\hbar/2m\omega)^2-C\hbar^2.$$

We have confined our attention to terms that are quadratic in v because the linear and constant terms lead to an unnecessary overdefinition of the resonance frequency.

Equation (2) is solved for the lower vibrational states using the generating function

$$\Phi(\xi,\eta,\zeta)=\sum_{v_1+v_2+v_3=v} b_{v_1v_2v_3}\xi^{v_1}\eta^{v_2}\zeta^{v_3},$$

where ξ, η, ζ are formal parameters. From (2), we have the following equation for Φ:

$$\varepsilon\Phi=\left\{\left(\alpha-\frac{\beta}{2}-\gamma\right)\sum_{s=\xi;\eta;\zeta}\left(s\frac{\partial}{\partial s}\right)^2\right.$$
$$\left.+\frac{\beta}{2}\left[\sum_{s=\xi;\eta;\zeta}s\frac{\partial}{\partial s}\right]^2+\gamma\left[\sum_{s=\xi;\eta;\zeta}s^2\right]\left[\sum_{s=\xi;\eta;\zeta}\frac{\partial^2}{\partial s^2}\right]\right\}\Phi, \tag{3}$$

and the solution of this is a polynomial of degree v. Table I lists the value of ε for $v=1, 2, 3, 4$ and different vibrational symmetries. It is clear from the table that, if we know the position of the $v=1$ and $v=2$ levels, we can determine the anharmonic constants α, β, and γ. For $v\gg 1$, the correction ε can be estimated approximately by including only the diagonal terms in the matrix $\hat{H}$:

$$\varepsilon=\alpha(v_1^2+v_2^2+v_3^2)+\beta(v_1v_2+v_2v_3+v_3v_1). \tag{4}$$

The correction to the energy, regarded as a function of v_1, v_2, and v_3, has three extrema, namely: $\varepsilon=\alpha v^2$, $\varepsilon=(\alpha+\beta)v^2/3$, and $\varepsilon=(2\alpha+\beta)v^2/4$. The first of these determines the position of the edges of the resulting energy band, and the last corresponds to its center of gravity (the trace of the matrix $\hat{H}$ divided by the number of levels in the band). The nondiagonal elements do not, therefore, affect the position of the band center. When the condition

$$\operatorname{sign}(\alpha\beta)=-1,\quad |\beta|>|\alpha|, \tag{5}$$

is satisfied, the band overlaps the position of the harmonic energy level. It is important to note that the inclusion of nondiagonal elements of the matrix $\hat{H}$ can lead only to an additional expansion of the band.

TABLE I.

v	Correction to energy	Level symmetry	
		T_d	O_h
0	0	A_1	A_{1g}
1	α	F_2	F_{1u}
2	$4\alpha+4\gamma$	A_1	A_{1g}
	$4\alpha-2\gamma$	E	E_g
	$2\alpha+\beta$	F_2	F_{2g}
3	$3\alpha+3\beta$	A_1	A_2
	$5\alpha+2\beta-2\gamma$	F_1	F_{2u}
	$7\alpha+\beta+\gamma\pm[(\beta+\gamma-2\alpha)^2+24\gamma^2]^{1/2}$	$2\times F_2$	$2\times F_{1u}$
4	$12\alpha+2\beta+2\gamma\pm2[(\beta+\gamma-2\alpha)^2+24\gamma^2]^{1/2}$	$2\times A_1$	$2\times A_{1g}$
	$12\alpha+2\beta-\gamma\pm[(2\beta-4\alpha-\gamma)^2+24\gamma^2]^{1/2}$	$2\times E$	$2\times E_g$
	$10\alpha+3\beta-6\gamma$	F_1	F_{1g}
	$8\alpha+4\beta+3\gamma\pm[(2\alpha-\beta+3\gamma)^2+24\gamma^2]^{1/2}$	$2\times F_2$	$2\times F_{2g}$

The spectrum of the triply degenerate mode of the molecule XY_4 with the symmetry T_d has been analyzed in a similar way. In this case, one must take into account cubic anharmonicity as well. However, this does not alter the form of the secular equation (2) and the condition given by (5).

Condition (5) is very likely to be satisfied for real molecules. Thus, the spectra of overtones and the composite vibrational modes of $ZrCl_4$ were obtained in[7]. It follows from these data that condition (5) is satisfied for the constants α and β. Our own measurements of the overtone spectra for the vibrational mode ν_3 of SiF_4 yield $\alpha\approx-2.5$ cm^{-1} and $\beta\approx 12$ cm^{-1}, which also satisfy the condition given by (5). Thus, the level bands for these molecules definitely overlap the "harmonic position" of the energy level.

We note that the formation of vibrational bands for molecules of the form XY_6, XY_4 with O_h, T_d symmetries is a consequence of the nonrandom Fermi resonance for the states of one vibrational mode. In addition to this type of Fermi resonance, polyatomic molecules exhibit Fermi resonances between levels corresponding to a particular symmetry type but belonging to different vibrational modes, independently of whether degenerate modes are present. This is connected with the fact that, as the energy of the vibrational state increases, there is an increase in the level density in this region. Fermi resonances of both types produce the mixing of vibrational states and the formation of vibrational level bands. Transitions between levels belonging to neighboring bands are allowed because of the anharmonicity of the molecular vibrations. The bands do not have sharp boundaries, but the transition strengths decrease between band centers and the edges. The case of degenerate vibrational modes differs from that of nondegenerate modes by the higher strength of dipole transitions and the greater width of the bands.

The spectrum of the triply degenerate vibrations of molecules with T_d or O_h symmetries is thus found to have a band structure. Since the size of a band and the degree of degeneracy increase in proportion to the square of the vibrational quantum numbers, on average, the level density in a band remains constant. When condition (5) is satisfied, the band overlaps the position of the harmonic level. Since dipole transitions within a band are allowed, we may conclude that this "net" of levels can ensure the cascade takeup of energy by the molecule. Moreover, since the density of levels belonging to all the modes of the polyatomic molecule increases rapidly with increasing vibrational energy, the above net of levels may substantially increase the dipole moments of intermode transitions as a result of the random Fermi resonances, and this may lead to an effective inclusion of a large number of levels belonging to other modes in the cascade process. It is clear that this effect may substantially facilitate the takeup of energy by the molecule.

2. The description of the excitation of high vibrational states of a molecule and the determination of the eigenvalues of its quasi-energy[8] can be carried out in the language of the "diffusion" approximation, based on the replacement of discrete variables and functions by continuous equivalents. Let us consider the "diffusion" equations for the ψ functions of a molecule in an external alternating field of constant amplitude $\mathbf{E}$. In the resonance approximation, the Hamiltonian has the form

$$\hat{H}=E_n\delta_{nm}+\mathrm{E}(\mathbf{d}_{nm}{}^{+}e^{-i\omega t}+\mathbf{d}_{nm}{}^{-}e^{+i\omega t}), \tag{6}$$

where $\mathbf{d}^{+}_{nm}$ and $\mathbf{d}^{-}_{nm}$ are the over- and sub-diagonal components of the dipole moment operator. If the spectrum E_n is localized in the neighborhood of $n\hbar\omega$, then we can confine our attention to the near-diagonal terms in $\hat{\mathbf{d}}$, i.e., assume that

$$\mathbf{d}_{nm}{}^{+}=\mathbf{d}f(n)\delta_{n,\,m-1},\quad \mathbf{d}_{nm}{}^{-}=\mathbf{d}f(n-1)\delta_{n,\,m+1},$$

where $\mathbf{d}$ is the characteristic dipole moment of the transition.

In accordance with the Floquet–Lyapunov theorem,[9] the evolution operator $U(t)$ for a system with the Hamiltonian given by (6) can be written in the form

$$U(t)=\hat{S}(t)\exp\hat{K}t, \tag{7}$$

where $\hat{K}$ and $\hat{S}(t)$ are constant and periodic operators, respectively. In our case,

$$\hat{K}=i\hbar\omega n\delta_{nm}. \tag{8}$$

The unitary operator $\exp\hat{K}t$ produces the transition to the quasi-energy representation. The operator $\hat{S}$ satisfies the equation

$$i\partial\hat{S}/\partial t=\hat{H}'\hat{S}, \tag{9}$$

where

$$\hat{H}_{nm}{}'=\delta_{nm}(E_n-n\omega)+(\mathbf{d}_{nm}{}^{+}+\mathbf{d}_{nm}{}^{-})\mathrm{E},\quad \hbar=1.$$

Equation (9) can be solved, at least in principle, with the aid of the well-known procedure described by

$$S_{nm}=\frac{1}{2\pi i}\int_{Q}(z-\hat{H}')^{-1}_{nm}e^{izt}\,dz, \tag{10}$$

where the integration contour Q runs around all the eigenvalues of the operator $\hat{H}'$. This procedure can be concluded in two interesting special cases, namely, $E_n=n\hbar\omega$, $f(n)=1$, $n\leqslant N$ and $E_n=n\hbar\omega$, $f(n)=\sqrt{n}$, $n\leqslant N$.[10] The first case corresponds to the N-level oscillator with equal transition dipole moments, and the second to the N-level harmonic oscillator.

However, in the more general case when $\{\Delta_n\}=\{E_n-n\hbar\omega\}\neq 0$ and $\mathbf{d}_{n,n+1}=\mathbf{d}f(n)\equiv\mathbf{d}_n$, the procedure represented by (10) is purely formal and is unsuitable for further calculations. To analyze (9), we must then write the equation for $\psi_n(t)=\sum_k S_{nk}(t)\psi_k(0)$ and confine our attention to a weak change in the transition dipole moment with level number such that $f'(n)\ll f(n)$:

$$i\frac{\partial\psi_n}{\partial t}=\Delta_n\psi_n+\mathbf{E}\mathbf{d}_n(\psi_{n-1}+\psi_{n+1}). \tag{11}$$

We must now proceed to the diffusion representation. To do this, we introduce the sufficiently smooth functions $d(\xi)$, $\psi(\xi)$, and $\Delta(\xi)$ such that

$$\mathbf{d}(n)=\mathbf{d}_n,\quad \psi(n)=\psi_n,\quad \Delta(n)=\Delta_n,$$

and replace the difference operator by a differential operator[11,12] as follows:

$$i\frac{\partial\psi(\xi)}{\partial t}=\Delta(\xi)\psi(\xi)+2\mathbf{E}\mathbf{d}(\xi)\,\mathrm{ch}\frac{\partial}{\partial\xi}\psi(\xi). \tag{12}$$

The boundary condition for (12) is $\psi(0,t)=0$. In the special case when $\mathbf{d}(\xi)\equiv\mathbf{d}$, the fundamental solution of (12) can be written in the form of the Feynman integral

$$\varepsilon(a,t_a,b,t_b)=\int_a^b\exp\left\{\int_{t_a}^{t_b}\left[\dot{x}\arcsin\dot{x}+(1-\dot{x}^2)^{1/2}-\frac{\Delta}{2\mathbf{E}\mathbf{d}}\right]2\mathbf{E}\mathbf{d}\,dt\right\}D(x). \tag{13}$$

The precise evaluation of this integral is not possible but the representation of the solution of (12) in terms of (13) may be useful for evaluating the corrections to the eikonal approximation[13] [see Eq. (18) below] and for the analysis of a system of levels with a substructure. Equation (12) can be reduced to the Schrödinger equation when

$$\Delta/2\mathbf{E}\mathbf{d}\ll 1. \tag{14}$$

This condition is satisfied for sufficiently strong fields, and essentially indicates that the entire domain of ξ is classically accessible. In this case, the quasi-energy levels z can be determined by expanding $\cosh\partial/\partial\xi$ in powers of $\partial/\partial\xi$ in the neighborhood of the origin, and writing (12) in the form

$$\frac{\partial^2}{\partial\xi^2}\psi=\left(\frac{\Delta-z}{\mathbf{E}\mathbf{d}}-2\right)\psi. \tag{15}$$

The eigenvalues of this equation determine the spectrum of quasi-energy $z<0$. Since the quantity $(\Delta-z)/\mathbf{E}\cdot\mathbf{d}-2)$ is, in effect, the potential energy, Eq. (15) and the requirement that $z<0$ signify that the quasi-energy level z lies at a distance less than $2\mathbf{E}\cdot\mathbf{d}$ from the bottom of the potential well, and this is a sufficient condition for the validity of the expansion in powers of $\partial/\partial\xi$.

To determine the quasi-energy level $z>0$, we can expand $\cosh\partial/\partial\xi$ in the neighborhood of $i\pi$. For $\tilde{\psi}_n=\psi_n e^{i\pi n}$, we then have

$$\frac{\partial^2}{\partial\xi^2}\tilde{\psi}=\left(\frac{-\Delta+z}{\mathbf{E}\mathbf{d}}-2\right)\tilde{\psi}, \tag{16}$$

and the eigenvalues of this equation determine the positive values of the quasi-energy spectrum. Thus, Eqs. (15) and (16) can be used to determine the approximate quasi-energies in fields that are strong enough for the dynamic Stark effect to compensate the detuning due to anharmonicity, right up to high vibrational states.

However, even in relatively weak fields, when condition (14) is not satisfied, qualitative analysis of (12) is possible on the basis of the quasiclassical approximation. To do this, let us write the Hamiltonian in the classical limit:

$$H'=2\mathbf{E}\mathrm{d}\cos p+\Delta. \tag{17}$$

In the first quasiclassical approximation (the eikonal approximation), we have

$$\psi_z=\exp\{iS_{\mathrm{cl}}(z)\}=C_1\exp\left\{i\int\arccos\frac{\Delta-z}{2\mathbf{E}\mathrm{d}}d\xi\right\}+C_2\exp\left\{-i\int\arccos\frac{\Delta-z}{2\mathbf{E}\mathrm{d}}d\xi\right\}, \tag{18}$$

where S_{cl} is the classical action. The expression given by (18) can be improved still further with the aid of perturbation theory and the integral over the trajectories given by (13). From (18) and from the asymptotic behavior of $\arccos x$ for $x\to\pm\infty$, it is clear that, in the case of large detuning

$$\psi_z=C_1\exp\left\{-\int\ln\frac{\Delta-z}{2\mathbf{E}\mathrm{d}}d\xi\right\}+C_2\exp\left\{\int\ln\frac{\Delta-z}{2\mathbf{E}\mathrm{d}}d\xi\right\}, \tag{19}$$

and this gives us an estimate for the population for highly detuned states $\psi_n\sim(2\mathbf{E}\cdot\bar{\mathrm{d}})^n(\overline{\Delta-z})^{-n}$, which agrees with that obtained, for example, in[3] on the basis of different ideas ($\bar{\mathrm{d}}$ and $\overline{\Delta-z}$ are the geometric averages of d and $\Delta-z$).

Thus, near the bottom of the well, the solutions of (12) are satisfactorily reproduced by solutions of the Schrödinger equation (15), (16), whereas, in the case of tunneling through a high barrier, or in the case of passage through a deep well, we have the approximation given by (19). It is clear from (19) that both a deep well and a high barrier lead to an exponential attenuation of the ψ function.

Before the rate of population of high vibrational states can be determined, we must know the time taken by a "particle" produced at the origin at time $t=0$ to reach the point $\xi=N$. The solution of the problem for "classically accessible regions" $|\Delta-z|\leqslant|2\mathbf{E}\cdot\mathrm{d}|$ can be obtained by the well-known procedure in which

$$\partial S_{\mathrm{cl}}/\partial z=\mathrm{const}, \tag{20}$$

which yields an estimate for the time taken to traverse the classically accessible region:

$$t_{\mathrm{cl}}=\int[(2\mathbf{E}\mathrm{d})^2-(\Delta-z)^2]^{-1/2}d\xi. \tag{21}$$

In classically inaccessible regions for which $|\Delta-z|>|2\mathbf{E}\cdot\mathrm{d}|$, the function S_{cl} can be used to determine the tunneling time[6]

$$t_t=\exp(-2\,\mathrm{Im}\,S_{\mathrm{cl}})=\left(\frac{\overline{\Delta-z}}{2\mathbf{E}\bar{\mathrm{d}}}\right)^{2n}\frac{1}{2\mathbf{E}\mathrm{d}_{n+1}}. \tag{22}$$

We note that this result is valid for any number of highly detuned levels. When the number of levels is $n\leqslant3$, the problem admits of an exact solution.[14]

The population distribution in an N-level system depends on the way in which the external field is introduced. There are two limiting cases: adiabatically slow, for which $\tau_f\gg\max(t_t,t_{\mathrm{cl}})$, and instantaneous, $\tau_f\ll\min(t_t,t_{\mathrm{cl}})$, where τ_f is the length of the laser pulse front. The characteristic feature of the instantaneous establishment of the field is the presence of beats, i.e., the "population flicker"[10] due to the simultaneous population of all the quasi-energy levels. The adiabatic establishment of the field leaves the system in the same quasi-energy level, but the level itself (its eigenvalue and eigenfunction) is slowly detuned, which leads to a certain stationary distribution of populations over the states of the molecule.

The Feynman integral can be used to generalize the results obtained for a set of single levels to that of a set of levels with a substructure. By substructure, we shall understand a set of sublevels with close energy values which can be reached only by transitions from the sublevels of other levels. Preliminary analysis shows that the principle of least action predicts that the cascade takeup of energy by the molecule is localized at levels detuned by more than $2\mathbf{E}\cdot\mathrm{d}$ from the harmonic energy.

Let us now summarize the main results of Sec. 2. Regions with $|z-\Delta|>|2\mathbf{E}\cdot\mathrm{d}|$ are classically inaccessible, and the tunneling time through them is given by

$$t_t\sim\frac{1}{2\mathbf{E}\mathrm{d}_{n+1}}\left(\frac{\overline{\Delta-z}}{2\mathbf{E}\bar{\mathrm{d}}}\right)^{2n}.$$

In classically accessible regions, we have (21), which enables us to estimate the parameters of motion over levels with small detuning.

3. To estimate the excitation efficiency, let us choose a particular form for the functions $\Delta(\xi)$ and $\mathrm{d}(\xi)$. We shall assume that the excitation is initially localized within the limits of a particular mode and that, in this region, $\mathrm{d}(\xi)\equiv\mathrm{d}_1\approx3\times10^{-19}$ cgs. In accordance with the results of Sec. 1, we shall suppose that, since anharmonicity does not accumulate, the detuning of the lower levels is restricted to values determined by the anharmonic constants of the molecule. Moreover, the inclusion of rotations and, consequently, the possibility of vibration–rotation transitions without a change in the rotational energy, or with a change by $\pm2BJ$ in this energy, leads to an increase by a factor of 3 in the level density for a given value of J. The maximum detuning Δ from resonance is $\Delta\approx\delta/6$, where δ is the separation between levels within the band, calculated in Sec. 1. For molecules such as SF_6 and SiF_4 the value of Δ does not exceed 1–2 cm^{-1}. It is important to note that the choice of the value of J is dictated by the laser field frequency and its variation within the linear-absorption band may lead to a substantial reduction and, possibly, complete compensation of detuning for several low-lying

levels.[5] The range of values of J covered by the field is, clearly, determined by the ratio $n_J \sim \mathbf{E}\cdot\mathbf{d}/BJ$.

However, even when anharmonicity is not compensated on the lower levels, the latter can be efficiently traversed as a result of the tunneling mechanism. According to (22) (Sec. 2), the tunneling time is determined by the probability of finding the system in the nth level and the rate of transition to a higher state:

$$t=\frac{\hbar}{2\mathbf{E}\mathbf{d}_2}\left(\frac{\hbar\bar{\Delta}}{2\mathbf{E}\mathbf{d}_1}\right)^{2(n-1)}.$$

The necessary condition for efficient traversal of the lower detuned levels in this case is that this time must be of the order of the laser pulse length. When $\tau_p \approx 10^{-7}$ sec, $\Delta \approx 1$ cm^{-1}, $\mathbf{d}_2 \approx 10^{-2}\mathbf{d}_1$, and $n=5$, the probability of traversing the set of detuned levels is close to unity when the intensity exceeds the threshold value $I_{\rm th}=20$ MW/cm^2. For intensities below this value, the probability of traversing the set of detuned levels is proportional to I^{n-1}.

Further increase in the quantum number due to an increase in the level density[3] and, consequently, in the probability of formation of random Fermi resonances between levels in a given band and those corresponding to other modes and composite vibrations, results in a reduction in detuning and the formation of a quasicontinuum. The transition dipole moment in the quasicontinuum, including the Fermi resonances, can be estimated from the expression $\mathbf{d}_2=\varkappa\mathbf{d}_1/\omega=10^{-2}\mathbf{d}_1$, where $\varkappa$ is the intermode anharmonic constant. Using (25) and restricting the energy takeup time to the laser pulse length τ_p, we can estimate the number of absorbed photons from the formula

$$N=\tau_p 2\mathbf{E}\mathbf{d}_2/\hbar.$$

For a pulse intensity of 10 MW/cm^2 and $\tau_p=10^{-7}$ sec, we have $N=150$. This is in agreement with experimental data on the dissociation of molecules during the excitation of degenerate vibrations.[5] These estimates also show that, even for intensities $I=10$ MW/cm^2, the process of cascade takeup of energy by molecules with vibrational degeneracy is very efficient. The net result is that the molecules take up a very large amount of energy (15 eV), much greater than the dissociation energy. However, in all probability, the breakup of the molecule is not at all a trivial problem. In fact, experiments on the dissociation of SF_6[5] show that the enrichment coefficient is very dependent on intensity (I^3) and this cannot be explained within the framework of the above energy takeup model. It would appear that, to explain this fact, one must consider the behavior of the molecules in the upper vibrational states.

In conclusion, let us consider a possible mechanism for the dissociation of a highly excited molecule in a laser field. We shall confine our attention to the dissociation of a molecule into two fragments. The vibrational energy of a molecule is then given by

$$\varepsilon_v=\varepsilon_1+\varepsilon_2+\varepsilon_{\rm kin},$$

where $\varepsilon_{1,2}$ is the vibrational energy of the first and second fragments, respectively, and $\varepsilon_{\rm kin}$ is their kinetic energy in the center of mass system. For a bound state, $\varepsilon_{\rm kin}<0$ and dissociation is not possible. The kinetic energy deficit can be compensated through the absorption of a photon of energy $\hbar\omega$, and the kinetic energy then becomes of the order of $\hbar\omega$. The dipole moment for a transition to a singlet state can then be estimated from the formula

$$|\mathbf{d}|=\int \psi_p^* \hat{\mathbf{d}} \psi_b \, dV,$$

where the wave function in the free state is $\psi_p \sim V^{-1/2}$ and the wave function for the bound state is $\psi_b \sim r^{-3/2}$; V is the quantization volume for translational motion, r is the amplitude of the molecular vibrations, $\mathbf{d}=e\hat{\mathbf{r}}$, and e is the effective charge of atoms in the molecule. This yields $|\mathbf{d}| \sim er^{5/2}V^{-1/2}$. In a laser field, the rate of transitions to the free states is $w=\hbar^{-1}\mathbf{d}\cdot\mathbf{E}\Delta n$, where $\Delta n \sim \mathbf{E}\cdot\mathbf{d}Vm\omega/\hbar^2 c$ is the number of free states "covered" by Stark broadening, and m is the reduced mass of the fragments. The final estimate for the dissociation probability is

$$w \sim \mathrm{E}^2 r^5 m\omega e^2 \hbar^{-3} c^{-1}.$$

The molecule will dissociate during the pulse length τ_p provided the energy density in the laser pulse satisfies the condition

$$I\tau_p \gg \hbar^3 c^2 (8\pi r^5 m\omega e^2)^{-1}.$$

For $r=0.5$ Å, $m=10^{-22}$ g, $\omega=10^{13}$ sec^{-1}, and $e=4.8\times10^{10}$ cgs, this is equivalent to the following order of magnitude result

$$I\tau_p \gg 5 \text{ J/cm}^2 .$$

We note that we have obtained only the lower limit for the threshold of instantaneous dissociation of an excited molecule in a laser pulse. In general, the threshold may, in fact, be higher if the effective charge e and the vibration amplitude r are somewhat lower than the values adopted above.

Thus, the above qualitative analysis suggests an additional dependence of the dissociation rate on laser field intensity.

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Effect of coherent radiation on the translational motion of atoms

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We consider the action of a traveling monochromatic wave on freely moving atoms having a transition that is at resonance with the light (between levels 1 and 2). A direct solution is obtained for the self-consistent quantum problem of the simultaneous effect of the field on the internal and external (translational) degrees of freedom. It is established that the effect of motion on the periodic variation of the populations of levels 1 and 2 (nutation) reduces to averaging the known solution (without allowance for the motion) over the momentum distribution, the form of which is the same as the initial one but the center of which is shifted by half the momentum of the traveling-wave photon. It is shown that if the momentum distribution is so narrow that the spread of the Doppler shifts is small in comparison with the nutation frequency, then the initial coordinate wave packet is divided by the light into two packets with different velocities, of which one spreads out more slowly than in the absence of the action of light, while the other spreads more rapidly. The conditions under which the spreading of the first packet is anomalously slow are obtained.

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1. INTRODUCTION

Monochromatic radiation that is at resonance with one of the atomic transitions causes periodic changes (nutation) in the populations of the levels that are included in the process. The dynamics of this process has been thoroughly investigated[1–4] neglecting the influence of the translational motion of the atom on the nutation and the effect of the nutation on the motion. The presence of translational motion leads to averaging of the nutation process over the distribution of the frequencies of the atomic transitions, which is the result of the Doppler shift. However, the initial momentum distribution, which is responsible for the Doppler broadening, is altered by the interaction, since the light-induced transitions between the resonant terms change in the momentum of the atom. In fact, the form of this distribution can be determined only by directly solving the self-consistent quantum problem of the simultaneous influence of the field on the internal and external (translational) degrees of freedom. The solution of this problem makes it possible not only to determine the influence of the translational motion on the dynamics of the nutation transitions, but also to describe the reaction of these transitions on the translational motion of the atoms.

In addition to the general physical importance of a rigorous solution of the problem of resonant interaction of light with atoms, this interaction is of interest also for some applications of laser optics. We have in mind, in particular, acceleration of atoms by resonant radiation,[5–10] which makes it possible to separate from atomic beams particles that are at resonance with the light field.

We consider in this paper the effect of a traveling monochromatic wave on freely moving atoms that have a transition resonant with the light. It is established that the effect of the motion on the light-induced transitions between two nondegenerate levels reduces to an averaging of the solution of the known nutation problem over the momentum distribution, the form of which is the same as the initial one, but the center is shifted by $\hbar k_0/2$ ($\hbar k_0$ is the momentum of the traveling-wave photon). We obtain the time evolution of the shape of the wave packet. It is shown that in the case of a sufficiently narrow initial momentum distribution, when the Doppler-shift spread due to the momentum uncertainty is small