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Mechanism of collisional dissociation of polyatomic molecules

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Recent experimental data are used as a basis for an analysis of the process of collisionless dissociation of molecules in a laser field. Some specific features of the vibrational-rotational spectrum of polyatomic molecules are established. The departure of molecules from the vibrational ground state independently of the rotational quantum number J is explained. A distribution is obtained for the density of vibrational states over the band for large vibrational numbers, and this is used to explain the large red shift of the optimum laser interaction during the dissociation stage of the process.

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1. Collisionless dissociation of polyatomic molecules in an infrared laser field has attracted considerable attention (a number of review articles has been published[1]). The subdivision of the vibrational excitation of polyatomic molecules into two stages[2] is now generally accepted. These two stages are: (1) traversal of several low-lying levels and (2) subsequent excitation in the so-called quasicontinuum, where the density of vibrational states is very high. It was originally assumed that the traversal of several low-lying vibrational levels occurred as a result of field broadening whereas the accumulation of energy in the quasicontinuum is definitely due to the high density of vibrational states and consequently, the resonant character of the process. Subsequent studies of the excitation of high-lying vibrational states showed that the resonant character of the transitions in the quasicontinuum is not in itself sufficient because these transitions occur with a considerable change in the vibrational quantum numbers and are, therefore, highly forbidden.

It has been shown[3] that, for symmetric molecules, intramode anharmonism, which removes the degeneracy of high-lying vibrational states of a degenerate mode, leads to the formation of bands of levels. Interband anharmonism ensures that band formation involves the states of other modes (Fermi resonance). The result of this is that bands of relatively well allowed transitions appear in the quasicontinuum, and the only forbidden transitions are those forbidden on the grounds of symmetry. The band structure of the quasicontinuum has, in fact, been confirmed experimentally.[4]

Recent experimental work suggest that the excitation of low-lying vibrational levels requires a more careful analysis. For example, Ambartsumyan *et al.*[5] have shown that the traversal of the low-lying levels in the case of the SF_6 molecule occurs in fields of moderate intensity (of the order of 100 kW/cm^2). Ambartsumyan *et al.* suggest vibrational compensation of anharmonism due to successive P, Q, and R transitions as the mechansim for the traversal of low-lying vibrational levels. However, this model is too schematic for a polyatomic molecule. We draw attention to the theoretical work of Larsen and Blombergen,[6] who pay considerable attention to the possibility of two- and three-photon resonances during the traversal of the low-lying vibrational levels.

However, the models mentioned above were based on the assumption that only particles in a narrow range of values of the rotational quantum numbers J participated in the excitation process. Recently, it was found experimentally[7] that the molecules could be removed from the vibrational ground state independently of their initial rotational state. It was shown that, in moderate fields of exciting radiation, beginning with $I = 300$ kW/cm^2, and for pulse lengths $\tau_p = 100$ nsec, the SF_6 and SiF_4 molecules can leave the vibrational ground state practically independently of J under conditions including rotational relaxation of the gas. This result is well outside the usual framework of the "bottleneck" effect.[8]

In this paper, we consider the mechansim responsible for the trapping of many rotational states during the vibrational excitation of molecules in a strong infrared field. We shall show that this trapping cannot be explained within the framework of the main vibrational transition alone, but is a consequence of the complicated structure of several low-lying vibrational levels as well as the presence of the quasicontinuum in the case of the polyatomic molecules. Even a considerable departure from the resonance, involving the intermediate vibrational-rotational levels, will not then prevent the effective population of the higher-lying vibrational states when the two-, three-, and so on, photon resonance conditions are satisfied.

Next, we shall consider the accumulation of energy by a molecule in the quasicontinuum, calculate the density of states in the bands, and explain the red-shift effect and the dependence of the energy accumulated by the molecule on the energy of the laser pulse.

2. In this section, we shall consider the spectrum of low-lying vibrational levels and will investigate the spectral width of two- and three-photon resonances by considering the particular example of SF_6, whose spectroscopic parameters have been adequately investigated. Consider an SF_6 molecule with a given quantum number J in the vibrational ground state. The 0–1 transition of the ν_3 mode of this molecule has three rotational branches (P, Q, and R). Anharmonism produces the splitting of the second and third vibrational states of ν_3 into three and four vibrational levels, respectively.[9] Resonant two- or three-photon transitions can take place to each of these states when the laser field frequency has the appropriate value. Moreover, each two-photon resonance has five rotational branches ($J = 0; \pm 1; \pm 2$), and each three-photon resonance has seven branches ($J = 0; \pm 1; \pm 2; \pm 3$). The result is that, for given J, the SF_6 molecule has 3 single-photon (Fig. 1a), 15 two-photon (Fig. 1b), and 28 three-photon (Fig. 1c) resonances of the mode ν_3.

When these spectra are recorded for a tunable laser with a linewidth of 0.03 cm^{-1}, the width of the observed resonances is determined by the Coriolis splitting of the vibrational-rotational state which, according to McDowell,[10] amounts to $0.0037J$ cm^{-1}, i.e., 0.17 cm^{-1} for $J = 50$. The figure of 0.03 cm^{-1} is characteristic for pulsed CO_2 lasers used in experiments on collisionless dissociation. This exceeds the mean separation between the Coriolis structure components.

The observed width of the resonances does not depend on the number of photons involved in the resonance because the Coriolis splitting increases linearly with the vibrational quantum number. Thus, it is clear that, for $J = 50$, the resultant width of two-photon resonances is 3 cm^{-1} and that of three-photon resonances is 6 cm^{-1}. The region in which the resonances exist is determined by the magnitude of the anharmonic splitting of the second and third vibrational states. The resultant relative overlapping of this region by the two- and three-photon resonance bands is close to unity. The region of existence of the resonances and the width of each of them increase with increasing J. The relative overlap does not, therefore, depend very much on J.

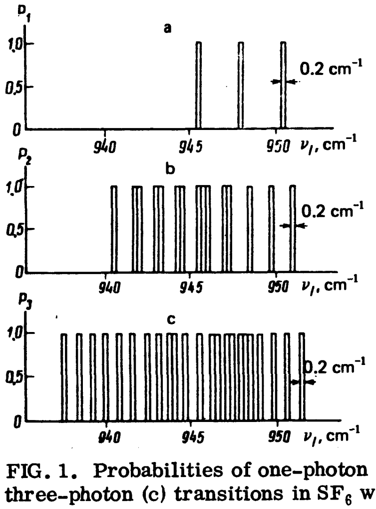

FIG. 1. Probabilities of one-photon (a), two-photon (b), and three-photon (c) transitions in SF_6 with rotational quantum number $J = 50$ as functions of laser frequency ν_l. The intramode anharmonic constants are chosen arbitrarily.

This leads us to the important conclusion that one can alway isolate a frequency band near the frequency of the main transition in which, for given laser frequency, all the particles will experience a two-photon or three-photon resonance with high probability and independently of their rotational state without, generally speaking, entering into resonance with the main transition. The width and structure of this region are determined by the spectrum of low-lying vibrational states and the gas temperature. Figure 2 shows the calculated dependence of the fraction of the total number of illuminated SF_6 gas molecules undergoing two-, photon (Fig. 2) and three-photon (Fig. 3) resonance as a function of the frequency of the exciting laser for gas temperatures of 300 °K and 50 °K, on the assumption of a thermal distribution of the particles over the rotational states.

The calculations were performed on a computer on the assumption that all the molecules were in the vibrational ground state, i.e., the influence of hot bands was ignored. The fraction of particles in the Q branches of the two- and three-photon resonances was determined by extrapolating spectroscopic data on the Q-branch widths of the main transition of the mode ν_3.[11] In the calculations of the fraction of molecules in the side branches of the two- and three-photon resonances, we took into account the dependence of the width of each resonance on J ($0.034J$ cm^{-1}), the statistical weight of these rotational states ($\sim J^2$), and the Boltzmann factor at the given temperature.

It is important to note that Stark broadening of the levels in the field was not taken into account. This broadening will obviously lead to an increase in the

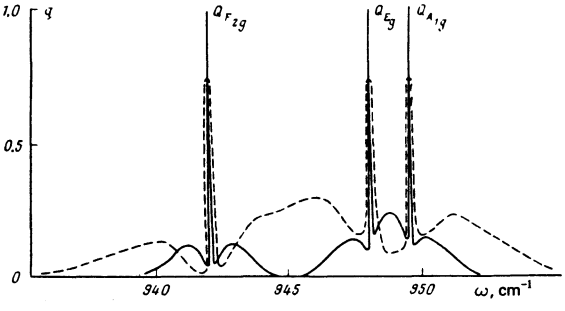

FIG. 2. Fraction of molecules undergoing two-photon resonance as a function of laser frequency (in the case of SF_6). Anharmonic constants $\alpha = 1$ cm^{-1}, $\beta = -12$ cm^{-1}, $\gamma = -0.5$ cm^{-1}. Broken curve—$T = 300$ °K, solid curve—50 °K.

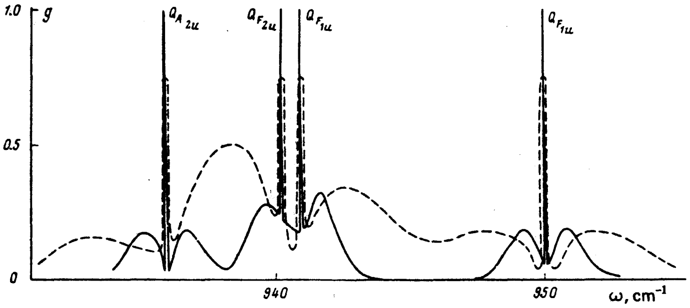

FIG. 3. Fraction of molecules undergoing three-photon resonance as function of laser frequency. Broken curve—$T = 300$ °K, solid curve—50 °K.

fraction q of the particles and to the smoothing of the curves in Fig. 2. This will be particularly appreciable when the magnitude of the Stark broadening is of the order of the width of each of the resonances, i.e., of the order of 0.2 cm^{-1} for SF_6. There is no doubt that the influence of hot bands at room temperatures leads to a considerable smoothing of the curves in Fig. 2. It will be clear from the ensuing analysis that these curves are essentially the resonance characteristics during the traversal of low-lying vibrational levels. It is precisely these curves that restrict the selectivity of the excitation. This selectivity is considerably enhanced when the gas temperature is reduced, but falls as the intensity of the exciting field increases.

3. In this section, we consider the efficiency of excitation of molecules detuned from the resonance on the main transition and undergoing two- or three-photon resonance. We shall assume that all the molecules undergo two- or three-photon resonance independently of their initial rotational state, and the detuning from resonance on the main transition for a given excitation frequency is determined by the magnitude of J.

We shall now consider the case of the two-photon resonance. Suppose that we have a system of three discrete levels, 0, 1, and 2, each of which is illuminated by laser radiation of frequency ω_l. The detuning of the 0–1 transition frequency from ω_l is Δ_1, and the detuning of the 0–2 transition from $2\omega_l$ is, in general, Δ_2. The dipole moments of the 0–1 and 1–2 transitions are d_1 and d_2, respectively. The probability amplitudes a_i (i labels the levels) in the approximation of slowly-varying amplitudes[12] are given by the solutions of the following equations:

$$i\hbar\frac{\partial a_0}{\partial t}=\frac{d_1E}{2}a_1, \tag{1.1}$$

$$i\hbar\frac{\partial a_1}{\partial t}=\Delta_1a_1+\frac{1}{2}d_1E^*a_0+\frac{1}{2}d_2Ea_2, \tag{1.2}$$

$$i\hbar\frac{\partial a_2}{\partial t}=\Delta_2a_2+\frac{1}{2}d_2E^*a_1. \tag{1.3}$$

The case $|\Delta_1| \leqslant 1/2|Ed_1|$, for which the 0–1 transition is in resonance with the laser field, presents a trivial situation. We therefore consider the case of large intermediate detuning $|\Delta_1| \gg |Ed_1|$ and $|\Delta_1| \gg |Ed_2|$. In this case, level 1 is practically unpopluated and, consequently, we have $|\hbar\partial a_1/\partial t| \ll \Delta_1 a_1$ in (1.2). If we use this condition, we can rewrite (1) in the form

$$-i\hbar\frac{\partial a_0}{\partial t}=\frac{|d_1E|^2}{4\Delta_1}a_0+\frac{d_1d_2E^2}{4\Delta_1}a_2, \tag{2.1}$$

$$i\hbar\frac{\partial a_2}{\partial t}=\left(\Delta_2-\frac{|d_2E|^2}{4\Delta_1}\right)a_2-\frac{d_1d_2}{4\Delta_1}a_0. \tag{2.2}$$

Neglecting, for simplicity, the change in E during the time of the pulse, and demanding that the two-photon resonance condition $4\Delta_2\Delta_1 = |Ed_1|^2 + |Ed_2|^2$ be satisfied, we obtain the following expression for the population of the upper level:

$$|a_2|^2=\sin^2(|d_1d_2E^2/4\hbar\Delta_1|t). \tag{3}$$

Thus, the population of the second level oscillates with the frequency

$$\Omega=|d_1d_2E^2/4\hbar\Delta_1|. \tag{4}$$

In practice, the vibrational-rotational levels of a molecule are degenerate in the component M of the angular momentum J along the direction of the field. Averaging over M leads to a rapid attenuation of the oscillations over one or two periods. This, in turn, leads to the equalization of the populations of the upper and and lower levels.[13]

We can now use (4) to determine the maximum intermediate detuning $\Delta_{1\max}$ for which the equalization of populations occurs during the time τ_p of the pulse:

$$\Delta_{1\max}=\pm|d_1d_2E^2/4\hbar|\tau_p. \tag{5}$$

Let us now suppose that the intensity of the laser field is $I = 10^5$ W/cm^2 and $d_1 = d_2 = 0.3D$, $\tau_p = 10^{-7}$ sec. Equation (5) yields $\Delta_1 = \pm 2$ cm^{-1}. These values of the dipole moments are characteristic for the SF_6 molecule. The region of intermediate detuning $\Delta_1 = \pm 2$ cm^{-1} contains eight P or R branch lines of the main 0–1 transition in the case of this molecule. Since SF_6 levels with $J > 80$ are practically unpopulated at room temperature, half of all the molecules undergoing two-photon resonance will be found to occupy the second level after the application of the laser pulse. It is clear from (5) that the trapping band and the number of excited molecules both increase in proportion to the pulse energy.

Let us consider the case of the three-photon resonance which may turn out to be an effective mechanism for the excitation of those particles for which the two-photon resonance condition is not satisfied. Suppose we have a four-level system in which the bottom level corresponds to the vibrational ground state with rotational quantum numbers J and M. The dipole moments of the 0–1, 1–2, and 2–3 transitions are, respectively, d_1, d_2, and d_3. The detunings from resonance for levels 1, 2, and 3 are, respectively, Δ_1, Δ_2, and Δ_3. Assuming that $|\Delta_1|$, $|\Delta_2| \gg |Ed_i|$, and Δ_3 satisfy exactly the three-photon resonance condition, we find that the population of the third level is

$$n_3=\sin^2(|E^3d_1d_2d_3/8\Delta_1\Delta_2\hbar|t). \tag{6}$$

Averaging over M as in the case of the two-photon resonance, and assuming that the equilibrium value $n_3=1/2$ is established after one or two oscillation periods, we find from (6) the maximum values of $\Delta=\Delta_1\approx\Delta_2$ for which the populations of the top and bottom levels become equal during the time of the pulse:

$$\Delta=\pm\left(\left|\frac{E^3d_1d_2d_3}{8h}\right|\tau_p\right)^{1/2}. \tag{7}$$

If we take $I=1$ mW/cm^2, $\tau_p=10^{-7}$ sec, and $d_1=d_2=d_3=0.3D$, we obtain $\Delta=\pm1.2$ cm^{-1}. In the case of SF_6, this band contains 50 lines belonging to the P or R branches, and this shows that the field is very effective in taking molecules with different J to the top state. It is clear from (7) that the width of the band increases in proportion to $I^{3/4}\tau^{1/2}$ in the case of three-photon resonance.

The above analysis was carried out without taking into account the upper vibrational states, and this may correspond to simple or asymmetric molecules. However, in the case of symmetric polyatomic molecules such as SF_6 or SiF_4, the irreversible trapping of particles into the higher vibrational state must be taken into account.

We now introduce the purely phenomenological probability w of this trapping process in the four-level scheme, assuming thereby that, beginning with the fourth level, the density of vibrational states is high enough to ensure that the quasicontinuous approximation can be employed.[2]

The set of equations for the probability amplitudes for the four low-lying levels is

$$i\hbar\frac{\partial a_0}{\partial t}=\frac{Ed_1}{2}a_1, \tag{8.1}$$

$$i\hbar\frac{\partial a_1}{\partial t}=\Delta_1a_1+\frac{d_2E}{2}a_2+\frac{d_1E^*}{2}a_0, \tag{8.2}$$

$$i\hbar\frac{\partial a_2}{\partial t}=\Delta_2a_2+\frac{d_3E}{2}a_3+\frac{d_2E^*}{2}a_1, \tag{8.3}$$

$$i\hbar\frac{\partial a_3}{\partial t}=-i\hbar wa_3+\frac{d_3E^*}{2}a_2. \tag{8.4}$$

We consider the following two limiting cases:

$$w\gg|E^3d_1d_2d_3/8\Delta_1\Delta_2|, \tag{9}$$

$$w\ll|E^3d_1d_2d_3/8\Delta_1\Delta_2|. \tag{10}$$

Condition (9) corresponds to the case of moderate fields when the frequency of the oscillations in the four-level system is less than the rate of removal to the upper states. In this case, the resultant population of the lower levels decays in accordance with the expression

$$\sum_{i=0}^{3}|a_i|^2=\exp\left[-\frac{2}{w}(d_1d_2d_3E^3/8\Delta_1\Delta_2)^2t\right], \tag{11}$$

which enables us to estimate the maximum detuning of the intermediate states for which the molecules efficiently escape to the upper vibrational states during the time τ_p of the laser pulse:

$$(\Delta_1\Delta_2)^{1/2}=|E^3d_1d_2d_3/8\hbar|^{1/2}(2\tau_p/w)^{1/4}. \tag{12}$$

When $I=1$ MW/cm^2, $\tau_p=10^{-7}$ sec, $d_1\approx d_2\approx d_3=0.3D$, and $w=0.7\times10^9$ sec^{-1} (see Sec. 4 below), the quantity $(\Delta_1\Delta_2)^{1/2}$ is equal to 1.5 cm^{-1}. A trapping band of this magnitude is sufficient for the field to take practically all the molecules into the quasicontinuum, independently of their rotational state.

Condition (10) is satisfied for strong fields, and the population of the lower levels decays in accordance with the expression

$$\sum_{i=0}^{3}|a_i|^2=e^{-wt}. \tag{13}$$

Within the framework of the problem formulated above, this case is less interesting because (10) signifies that the quasicontinuum begins with the third level for high intensities (see Sec. 4).

In this section, we consider the removal of the molecules to the upper vibrational states, the efficiency of this process, and its dependence on the laser field frequency. The high-lying vibrational levels form a continuum because of the high density of states. By a quasicontinuum we understand a density of states for which the separation between neighboring levels is less than the Stark broadening.[2] To describe the process of energy accumulation in the quasicontinuum, Akulin *et al.*[2] used the model of isolated levels close to resonance, but a physically more correct model must take into account the presence of a large number of closely spaced states. The dynamics of the population of such a system depends on the statistics of the matrix elements of the transition dipole moments. If the phases of the dipole moments are random, the kinetic equation becomes valid. A rigorous derivation of this equation can be based on the Zwanzig method.[14] We discuss below the range of validity of this method.

When Stark broadening is greater than the level separation, the transition probability in first-order perturbation theory can be calculated from the formula used for transitions in the continuum[12]

$$w_{ik}(\varepsilon_i,\varepsilon_k)=|Ed_{ik}|^2g(v\hbar\omega)\delta(\varepsilon_i-\varepsilon_k-\hbar\omega), \tag{14}$$

where $g(\epsilon)$ is the density of vibrational states. Accordingly, the population of the quasicontinuum is localized on levels in the neighborhood of $v\hbar\omega$. If we sum the entire perturbation-theory series, we can show that the δ function must be replaced by the Lorentz curve with width

$$|\overline{Ed_{ik}}|^2g(v\hbar\omega).$$

To estimate w, we must take into account the band character of the vibrational spectrum of polyatomic molecules.[3] The point is that, in polyatomic molecules with degenerate vibrations, bands of levels of width of the order of $\gamma_v \sim \alpha v^2$, where α is the characteristic anharmonic constant of the molecule, are formed in the neighborhood of the harmonic energy as a result of anharmonism. We shall assume that the dipole moment of transitions allowed on the grounds of symmetry between all the levels in neighboring bands is roughly the same. If a band with vibrational quantum number v contains N_v levels, the sum rule for the squares of the dipole moments shows that the absolute magnitude of the partial dipole moment of a transition from a level in one band to a level in a neighboring zone is $d_x \approx d_{01} v^{1/2} N_v^{-1/2}$. The density g_v of levels in a band can be estimated from the ratio of the number N_v of levels in the band to its width γ_v:

$$g_v \approx \gamma_v^{-1} N_v = \alpha^{-1} v^{-2} N_v.$$

The resultant kinetic coefficient of a transition from a band to a band is

$$w(v) \approx |Ed_{01}|^2 v N_v^{-1} g_v \sim v^{-1},$$

so that, when the laser field intensity is $I = 1$ MW, $\alpha = 3$ cm^{-1}, and $d_{01} = 0.3D$, this expression yields $w \approx 0.7 \times 10^9$ sec^{-1} for the fourth level. This was the figure used at the end of the last section.

The criterion for the validity of the kinetic equation is the condition that the $w(v)$-neighborhood of the energy $v\hbar\omega$ contains a large number of levels, i.e., $wg_v \gg 1$. This is equivalent to the condition for the existence of a quasicontinuum

$$Ed_x(v) g_v \gg 1. \tag{15}$$

Both $d_x(v)$ and $g(v)$ depend on the vibrational number v. The character of these functions is determined by the number s of degrees of freedom participating in the formation of the band of levels. In fact, the number of levels is $N_v \sim v^{s-1}$ and, consequently, $g_v \sim v^{s-3}$ and $d_x \sim v^{1/2} N_v^{-1/2} \sim v^{1-s/2}$ in accordance with the sum rule for the squares of the dipole moments. Hence, it is clear that, when $s = 4$, the condition given by (15) is not violated whereas, for $s > 4$, it becomes more stringent as the vibrational excitation increases. The degree of degeneracy of a mode of the polyatomic molecule does not exceed three. However, in the case of spherical-top type molecules, a further degree of freedom appears as a result of the removal of K degeneracy.[10] Moreover, the characteristic situation for polyatomic molecules is that where, in addition to the modes which resonate with the laser radiation, there are modes with frequencies $\omega/2, \omega/3$ which participate in the Fermi resonances with levels of the excited mode and take part in the formation of bands. Thus, in the case of SF_6, there is the triply degenerate mode $\nu_6 \approx \nu_3/3$. If we take these modes into account, the criterion for the validity of the kinetic equations for characteristic intensity values turns out to be satisfied even for the third or fourth level.

Thus, the kinetic equation

$$\frac{\partial \rho_v}{\partial t} = w(v+1)(\rho_{v+1} - \rho_v) - w(v)(\rho_v - \rho_{v-1}), \tag{16}$$

is valid within the limits of the above criteria, where ρ_v is the population of the band v. This equation can be conveniently solved by using the diffusion approximation

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial v} w(v) \frac{\partial}{\partial v} \rho. \tag{17}$$

The transition probability $w(v)$ then takes on the significance of a diffusion coefficient.

In the approximation adopted above, in which the dipole moments of the transitions between levels belonging to neighboring bands are constant, and the level densities are distributed uniformly within the band, the diffusion coefficient w is given by

$$w(v) \sim E^2 v^{-1}. \tag{18}$$

In this case, the solution of the diffusion equation (17) can be used to obtain the energy $\mathscr{E}$ accumulated by the molecule as a function of the energy of the laser pulse:

$$\mathscr{E} \sim \left(\int I dt \right)^{1/3}, \tag{19}$$

and this is in qualitative agreement with experiment.[15]

However, to obtain more accurate results, we have to carry out a more detailed analysis of both the level distribution in the band and of the transition dipole moments. As a first step in this direction, let us determine the level density in the band for a triply degenerate mode. In the quasiclassical approximation, this is given by

$$g_v(\varepsilon) = \iiint_0^v dv_1\, dv_2\, dv_3\, \delta(v_1 + v_2 + v_3 - v)\, \delta[\varepsilon - \alpha(v_1^2 + v_2^2 + v_3^2) - \beta(v_1 v_2 + v_2 v_3 + v_1 v_3)]$$

$$= \begin{cases} \dfrac{2\pi}{3^{1/2}|\beta - 2\alpha|}, & \dfrac{\alpha+\beta}{3} v^2 \leqslant \varepsilon \leqslant \dfrac{2\alpha+\beta}{4} v^2, \\[2ex] \dfrac{2\pi}{3^{1/2}|\beta-2\alpha|} \left[1 - \dfrac{3}{\pi} \arccos \left(\dfrac{|\beta - 2\alpha| v^2}{4(3\varepsilon - \alpha v^2 - \beta v^2)} \right)^{1/2} \right], & \dfrac{2\alpha+\beta}{4} v^2 \leqslant \varepsilon \leqslant \alpha v^2 \end{cases} \tag{20}$$

where ϵ is the detuning from the harmonic position of

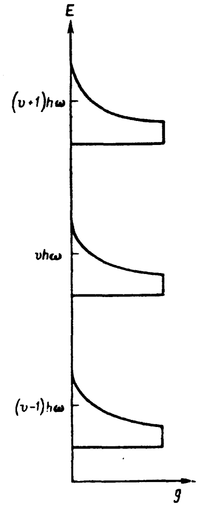

FIG. 4. Level density g in band with large ($v \gg 1$) vibrational quantum numbers when the harmonic energy falls into the band.

the energy and α and β are the intramode anharmonic constants. Figure 4 illustrates this schematically for $\alpha > 0$ and $\beta < -\alpha$. It is clear from this figure that the level density is a maximum between the red end of the band and its center of gravity, and decreases toward the blue end.

The above preliminary analysis leads to the following conclusions. The application of laser radiation at a frequency close to the frequency of the main transition is not the optimum procedure from the point of view of accumulation of energy in the quasicontinuum. The character of the density of states and hence of the diffusion coefficient changes with increasing vibrational excitation. This leads to a change in the exponent in (19). For example, if the dependence of the diffusion coefficient on v is $w \sim v^{-A}$, where A is some number, then, by solving the diffusion equation in (17), it can be shown that the energy accumulated by the molecule is given by

$$\mathscr{E} \sim \left(\int I dt\right)^{1/(2+A)}, \tag{21}$$

where I is the laser field intensity. From the point of view of traversing the quasicontinuum, the optimum situation is that in which the molecule is illuminated by radiation of frequency shifted toward the red by a considerable amount relative to the frequency of the main transition, where the density of the vibrational states is a maximum.

The above conclusions are illustrated in Fig. 5a. The parabolas in this figure correspond to the positions of the upper ($\epsilon = v^2$) and lower [$\epsilon = 1/3(\alpha+\beta)v^2$] edges of the band, and the parabola shown by the broken curve corresponds to the center of gravity of the band $\epsilon = 1/4(2\alpha+\beta)v^2$. The dotted curve corresponds to the optimum frequency of the exciting field when $v = 3$ is the starting level. The slope of the straight line determines the detuning Δ of the optimum frequency of the main transition. Excitation at the frequency of the main transition corresponds to the v axis.

Moreover, Fig. 5a shows the level-density distribution g in the tenth and twentieth band. For the chosen values of the anharmonic constants ($\alpha = 1\ \mathrm{cm}^{-1}$ and $\beta = -12\ \mathrm{cm}^{-1}$), the red shift of the optimum frequency is $50\ \mathrm{cm}^{-1}$, which is in good agreement with experimental results.[4]

It is clear from the above discussion that the red shift depends on the anharmonic constants of each molecule. However, there is no unique way of determining the anharmonic constants from the red shift. Figure 5b shows the positions of levels corresponding to the mode ν_3 for $\alpha = -4\ \mathrm{cm}^{-1}, \beta = 1\ \mathrm{cm}^{-1}$. In this case, the levels belonging to this mode are taken out of resonance by the field, and the accumulation of energy by the molecule can occur at the frequency of the main transition only by connecting levels of other modes to this band. When the red shift of the laser frequency corresponding to the second stage is $\Delta \sim 20-50\ \mathrm{cm}^{11}$, the detuning of the mode ν_3 is compensated and the excitation of the molecules may turn out to be more effective because of the larger transition dipole moments.

5. The above analysis thus enables us to describe the leading features of collisional dissociation of polyatomic molecules. These features are determined by the specific excitation of a few low-lying levels and the subsequent population of the set of high-lying vibrational states. Polyatomic molecules generally are characterized by a high density of vibrational-rotational states and this plays a fundamental role for both the low-lying and high-lying vibrational levels. In fact, the density of two- and three-photon resonances, averaged over the ensemble, is high for the low-lying vibrational levels. This ensures that a substantial fraction of the molecules illuminated by fields of moderate intensity (0.1 –1 MW) will absorb two or three photons independently of the positions of the intermediate levels with a probability of one-half. This situation may be realized in complex (SF_6, SiF_4, BCl_3) and relatively simple (D_2O) nonsymmetric polyatomic molecules. The excitation selectivity of the molecules is determined by the complex structure of a few low-lying vibrational levels. To increase this selectivity, the molecules must be cooled and the minimum possible laser intensity must be used during the first stage of the excitation process.

In the case of complex polyatomic molecules with degenerate vibrations, one has to consider the possibility of a further escape into the quasicontinuum. This ensures that practically all the molecules enter the region of the quasi-continuum under the action of the laser

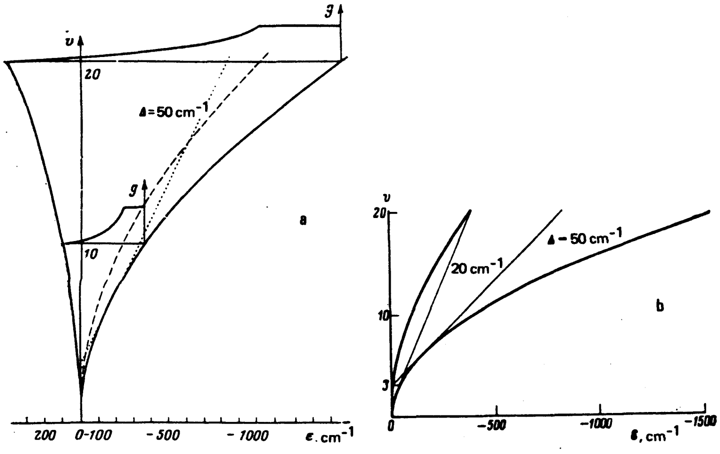

FIG. 5.

field. For molecules for which the formation of the quasicontinuum involves the participation of not less than four degrees of freedom, further accumulation of energy is described by the kinetic equation. The rate at which the energy accumulates is very dependent both on the density of vibrational states in the neighborhood of the excited levels and on the magnitudes of the dipole moments of the corresponding transitions. The removal of degeneracy and Fermi resonances lead to the formation of bands of relatively well-allowed transitions in the quasicontinuum. Efficient accumulation of energy in the quasicontinuum requires a large red shift of the laser field frequency relative to the resonance 0-1 transition.

We note in conclusion that the above analysis refers to two stages of collisionless dissociation of molecules, namely, traversal of the low-lying levels and the accumulation of energy in the band structure of the quasicontinuum of high-lying vibrational states. The process of only the dissociation of highly excited polyatomic molecules requires a separate analysis.

We also note that problems connected with the effect of laser radiation on the vibrational degrees of freedom of molecules were first discussed by Askar'yan[16] and Bunkin *et al.*[17]

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Resonance fluorescence in x-ray *K* spectra

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An analysis is made of the special features of the characteristic *K* x-ray fluorescence spectrum when the excitation is provided by an emission line of some element B, and the energy of this line coincides with the *K* absorption edge (lies within the natural width of the edge) of the investigated element A. It is shown that the *K* x-ray emission lines of the elements A are shifted toward lower energies and have profiles different from the usual Breit-Wigner shape. This effect has to be allowed for in precision measurements of the x-ray line energies and in studies of other effects associated with small line shifts (such as the chemical and isotopic shifts).

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INTRODUCTION

The processes associated with the excitation of an atom by electromagnetic radiation of frequency close to the resonance frequency of the atom and with the subsequent emission of light are well known in optics and are called resonance fluorescence.[1] A characteristic feature of these processes is that the profile and width of the emission (fluorescence) line depend strongly on the distribution of the primary radiation.

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