Analysis of models of radiative dissociation of polyatomic molecules in the field of laser radiation

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It is shown that allowance for rotation leads to an appreciable increase of the laser-radiation frequency interval in which effective excitation of a molecule is possible. The developed theoretical model, in which there are no free parameters, is in good quantitative agreement with the available experimental data for SF_6. Predictions are made concerning the relations between the characteristic dissociation parameters, and the possibility of their exponential verification is discussed. A method of quasistationary states is developed for a nonlinear oscillator in the Appendix.

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1. INTRODUCTION

According to experimental data,[1–7] vibrational modes of some polyatomic molecules (BCl_3, SF_6, and others) are excited by a laser-radiation field within a time shorter than the collision time, after which they dissociate. The most interesting aspects of this phenomenon is perhaps the excitation of the molecules to vibrational levels with small values of the vibrational quantum number $n \approx 3-5$, since this excitation should be strongly hindered by the anharmonicity of the oscillations. The anharmonicity presents no substantial obstacles to further excitation, for in the case of a polyatomic molecule it can be offset by the large level density in the upper quasicontinual section of the molecule energy spectrum.

Molecule vibrations induced by an external force have been discussed in the literature since the middle sixties.[8–9] It has been customary to use the model of a one-dimensional quantum nonlinear oscillator, which describes well the first stage of the molecule excitation, when the treatment can be restricted to one vibrational degree of freedom. The question of the first stage of excitation of the molecule has recently been intensively investigated theoretically using analytic[10–34] and numerical[35–39] methods. It is interesting to note that in most papers devoted to this question it is stated that a quantitative agreement exists between the theoretical model and the available experimental data.

In the present paper we also consider a certain theoretical model and arrive at an agreement with experiment. In addition, we do something which, unfortunately, the authors of almost none of the papers cited above did. In developing the models proposed by them, we formulate theoretical predictions that can be confirmed or denied experimentally. The latter is all the more desirable, since the predictions made within the frameworks of different models contradict one another.

In Appendix I we consider the excitation of a quantum nonlinear oscillator, using the method of quasistationary (or quasi-energy) states.[40,41] This enables us to obtain in a unified manner a number of results previously obtained by a variety of procedures, and correct the errors incurred there. In addition, in Appendix II we estimate the influence of the width of the laser-radiation spectrum on the system excitation.

2. COHERENT MULTIPHOTON TRANSITIONS

2.1. We consider a one-dimensional quantum nonlinear oscillator with energy spectrum

$$E(n)=\hbar(\omega_{01}+{}^1\!/_2\alpha)n-{}^1\!/_2\hbar\alpha n^2, \tag{1}$$

where ω_{01} is the frequency of the $0\to1$ transition and α is the anharmonicity constant. We introduce the field broadening f and the frequency detuning $\delta\omega$; let

$$f=Ed_{01}/\hbar, \quad \delta\omega=\omega_l-\omega_{01},$$

where d_{01} is the dipole moment of the $0\to1$ transition, E is the intensity of the laser field $E(t)=E\cos\omega_l t$, acting on the oscillator. Let the oscillator at the instant $t=0$ be in a state with $n=0$ and let the laser frequency ω_l be such that

$$E(n)-E(0)=\hbar\omega_l n. \tag{2}$$

If

$$n>4(f/\alpha)^{2/3}, \tag{3}$$

then the degree of cancellation of the anharmonicity by the field broadening turns out to be insufficient to populate the levels (2)[33] (it is understood that $n>1$). Nonetheless, when full account is taken of the quantum effects, the anharmonicity cannot prevent the population of the levels (2), even in the case (3). The anharmonicity can only greatly increase the time necessary to produce at the levels (1) a population comparable with unity. According to[27], in the case $\alpha^{1/3}f^{2/3}\ll|\delta\omega|\ll f$ this time is of the order of

$$t_{0n}\approx\frac{4\pi}{\alpha(n-1)}\exp\left\{\frac{B({}^5\!/_8,{}^3\!/_2)}{2}\left(\frac{\alpha}{f}\right)^{1/2}(n-1)^{7/4}\right\}. \tag{4}$$

The population of the levels (2) was considered in[20–22] for the case $f\ll\alpha$. Bloembergen and co-authors[22] have shown that the populations of the levels 0 and n will vary periodically with time:

$$p_n(t)=p_n\sin^2\left(\frac{\pi}{2}\frac{t}{t_{0n}}\right), \quad p_0(t)\approx1-p_n(t),$$

where

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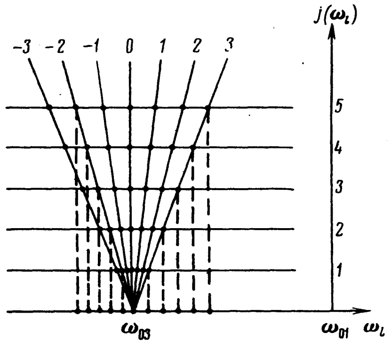

FIG. 1. Diagram for the determination of the resonance frequencies with rotation taken into account. The numbers on the curves indicate the values of Δj.

$$t_{0n}=\hbar\pi[\hbar^2n^2(\omega_l-\omega_l(0;\ n))^2+4|\Delta_{0n}|^2]^{-1/2}, \tag{5}$$

$$p_n=4|\Delta_{0n}|^2[\hbar^2n^2(\omega_l-\omega_l(0;\ n))^2+4|\Delta_{0n}|^2]^{-1}. \tag{6}$$

Here $\omega_l(0;n)$ is the resonant value of the laser frequency:

$$\omega_l(0;\ n)\equiv[E(n)-E(0)]/\hbar n,$$

$$\Delta_{0n}=V_{01}V_{12}\ldots V_{n-1n}\Big/\prod_{k=1}^{n-1}\Delta_k=\frac{(-1)^{n-1}}{2}\hbar\alpha\left(\frac{f}{\alpha}\right)^n\frac{n^2}{(n!)^{3/2}}; \tag{7}$$

$\Delta_k = E_k - E_0 - \hbar\omega_l k$, V_{pp+1} is the matrix element of the operator $\hat{V} = -E\hat{d}/2$, where E is a c-number. In the derivation of (4)–(6) it was assumed that the dipole-moment operator has nonzero matrix elements only for the transitions $n \to n \pm 1$. Therefore the results of formulas (5) and (6) are obtained only in n-th order perturbation theory.

In the case of a two-level system, when $n = 1$, formulas (5)–(7) describe, as is sometimes stated, the Rabi precession (see, e.g., [43], § 40). If $n > 1$, then it must be assumed that the population on the n-th level is the result of a coherent multiphoton transition.[26] The difference between the coherent and incoherent transitions manifests itself, in particular, in the fact that the characteristic time of the level population in the $0 \to n$ transition varies in the former case like $I^{n/2}$ and in the latter case like I^n, where I is the radiation intensity. In the case $n \gg 1$ and $f \gg \alpha$ the coherent multiphoton transition should be treated quasiclassically as tunneling in energy space.[27]

It was assumed above that the laser radiation is monochromatic. Actually the laser spectrum has a finite width $\Delta\omega_l$. The laser radiation can then be represented by a model consisting of the sequence of wave trains with frequencies ω_l and durations $t_{\text{coh}} = 2\pi/\Delta\omega_l$, which replace one another with a random change of the radiation phase. According to the results of Appendix II, the population of the n-th level reaches a value comparable with unity during the laser-pulse time t_{pulse} if

$$t_{0n}\leqslant\sqrt{t_{\text{coh}}t_{\text{pulse}}}, \tag{8}$$

where $t_{\text{coh}} \approx 2\pi/\Delta\omega_l$ is the time of the coherence of the radiation.

2.2. Let us calculate the effect of molecule location on the resonant frequencies. We write in place of (1)

$$E(n,j)=\hbar(\omega_{01}+{}^1\!/_2\alpha)n-{}^1\!/_2\hbar\alpha n^2+Bj(j+1);$$

the resonant frequencies are then

$$\omega_l(0,j;n,j+\Delta j)\equiv\frac{E(n,j+\Delta j)-E(0,j)}{\hbar n}\approx\omega_l(0;n)+\frac{2B}{\hbar}j\frac{\Delta j}{n}, \tag{9}$$

and Δ_{0n} will be different from zero in n-th order perturbation theory if $|\Delta f| \leqslant n$. By virtue of (9), the resonant values of $\Delta\omega_l$ will be those for which the quantity

$$j(\omega_l)\equiv\frac{\hbar(\omega_l-\omega_l(0;n))}{2B}\frac{n}{\Delta j}$$

is equal to a non-negative integer (it is understood that $\Delta\omega_l \ll 2Bj/\hbar n$). A plot of $j(\omega_l)$ for specified values of Δj is shown schematically in Fig. 1 for the case $n = 3$; the points show some resonant frequencies corresponding to $\Delta j = n$ and $\Delta j = -n + 1$.

Since the levels $j \leqslant (T/B)^{1/2}$ are populated at the temperature T, it is necessary to stipulate additionally that $j(\omega_l) \leqslant (T/B)^{1/2}$. We see that a large number of resonant frequencies appear when the rotation is taken into account. They are symmetrical about the frequency $\omega_l(0;n)$ in an interval of width

$$4(TB)^{1/2}/\hbar. \tag{10}$$

We note that at the temperature T the width $\Delta\omega_r(T)$ of the rotational bands of the molecule spectrum is half as large as (10).

The matrix element of the transition $|n, j\rangle \to |n + \Delta n, j + \Delta j\rangle$ depends on the rotational quantum numbers. We shall not consider here this dependence in detail. It is taken into account below by the fact that we use an experimental value[42] of the dipole moment d_{01} obtained at temperatures $T \approx 300$ °K.

3. ANALYSIS OF THEORETICAL MODELS

3.1. The probability W of the dissociation of an isolated molecule in the laser-radiation field depends, in particular, on the following parameters: the laser frequency ω_l, the width $\Delta\omega_l$ of the laser spectrum, the intensity I of the radiation, and the temperature T of the irradiated gas. Let $\Delta\omega_l$, I, and T stay constant; W as a function of ω_l has a maximum at a certain optimal frequency $\omega_{l\,\text{opt}}$. The corresponding frequency detuning will be designated $\delta\omega_{\text{opt}} = \omega_{l\,\text{opt}} - \omega_{01}$; obviously, $\delta\omega_{\text{opt}}$ depends on I, $\Delta\omega_l$, and T.

Let us examine the $\delta\omega_{\text{opt}}(\Delta\omega_l, I)$ dependence. Under certain conditions (see Sec. 3.3 below), the optimal value of the frequency ω_l is the one which makes it possible to populate within a time t_{pulse} the vibrational level with the maximum possible value of n. During the time t_{pulse} there can be populated only levels satisfying the condition (8). Denoting by N the maximum permissible value of n and taking (8) into account, we obtain

$$\left(\frac{f}{\alpha}\right)^n \frac{2n^2}{(n!)^{3/2}} \geqslant \frac{2\pi}{\alpha(t_{\text{coh}}t_{\text{pulse}})^{1/2}}. \tag{11}$$

Using the approximate equality

$$2N^2/(N!)^{3/2} \approx 30/(10)^{N/2},$$

which is accurate enough in the interval $n = 2-4$, and introducing the notation

$$I_\alpha = \frac{c}{8\pi}\frac{\hbar^2\alpha^2}{d_{01}^2},$$

we obtain

$$N = 2\lg\left(\frac{30\alpha(t_{\text{coh}}t_{\text{pulse}})^{1/2}}{2\pi}\right) \Big/ \lg\left(\frac{10I_\alpha}{I}\right). \tag{12}$$

Here we are already considering N to be a continuous parameter. To each value of N we set in correspondence an optimal frequency $\omega_{l\,\text{opt}} = \omega_l(0; n)$. This yields the dependence of $\delta\omega_{\text{opt}}$ on $\Delta\omega_l$ and I:

$$\delta\omega_{opt}(\Delta\omega_l, I) = -\alpha(N-1)/2, \tag{13}$$

where N is given by (12).

The dependence of the population that appears on the level n after a time t_{pulse} on I has a threshold (see (31) below). For this reason, $\delta\omega_{\text{opt}}$ can have a jumplike dependence on I. Such a dependence can be described by formulas (12) and (13) if N is taken to mean the integer part of expression (12).

We denote by $\Delta\omega_d$ the width of the dissociation spectrum, i.e., the interval in which W differs little from its maximum value. According to (10), $\Delta\omega_d$ depends on the temperature in the same manner as $\Delta\omega_r$, with

$$\Delta\omega_d = \frac{4}{\hbar}\sqrt{BT} = 2\Delta\omega_r. \tag{14}$$

The quantities $\delta\omega_{\text{opt}}$ and W should have a weak dependence on the temperature:

$$\delta\omega_{opt}(T),\ W(T) \approx \text{const}. \tag{15}$$

The dissociation probability is taken here at the detuning $\delta\omega = \delta\omega_{\text{opt}}$.

Thus, the model in which the anharmonicity is suppressed by a coherent multiphoton transition and the rotation causes the broadening of the dissociation spectrum leads to the relations (13)–(15).

3.2. The SF_6 molecule, whose dissociation was investigated in detail in[3–7], is characterized by the following constants (ν_3 vibration): $\alpha = 7$ cm^{-1}, $B = 0.055$ cm^{-1}, and $d_{01} = 0.3$ D. The value observed in[6] at $I \approx 3\times10^7$ W/cm^2, $\Delta\nu_l = 0.035$ cm^{-1} and $T = 300\,^\circ$K ($\Delta\nu = \Delta\omega/2\pi c$) is

$$\delta\nu_{opt} = -7\ \text{cm}^{-1},\ \Delta\nu_d \approx 18\ \text{cm}^{-1}. \tag{16}$$

At a laser pulse duration $t_{\text{pulse}} \approx 100$ nsec, formulas (13) and (14), in which there are no free parameters, yield values $N = 3.1$

$$\delta\nu_{opt} = -7{,}35\ \text{cm}^{-1},\ \Delta\nu_d = 14\ \text{cm}^{-1}; \tag{17}$$

In this case $I_\alpha = 2.6\times10^9$ W/cm^2 and $f = 0.76$ cm^{-1}.[1)] The agreement between the experimental (16) and theoretical (17) values is quite good. It would be all the more of interest to verify experimentally relations (13)–(15) in a wide range of values of I and T.

3.3. The dependence of W on I and $\Delta\omega_l$ is determined by the rate of excitation of the molecule after one of the vibrational modes has been excited to a certain critical level n_{cr}, starting with which the polyatomic characteristics come into play and the anharmonicity does not prevent further excitation of the molecule.[18] There are grounds for assuming that $n_{\text{cr}} = 3$ for symmetrical polyatomic molecules. Since the singularities of the behavior of the molecules at the levels $n > 3$ are not very well known presently, the dependence of W on I and $\Delta\omega_l$ cannot be reliably determined. We note only that if the rate of excitation at high levels is large enough, then the optimal laser frequency ω_l is the one at which $\omega_l = \omega_l(0; n_{\text{cr}})$. It follows therefore that in this case

$$\delta\omega_{opt}(I) = -\alpha(n_{cr}-1)/2 \approx \text{const}. \tag{18}$$

On the other hand, if the rate of excitation to the higher levels is low, then the optimal frequency ω_l is the one that makes it possible to reach the maximum vibrational number N within the time t_{pulse}. This yields relation (13). The excitation of a molecule to high levels can proceed by energy transfer from the mode built up by the laser radiation into other modes as a result of equality of the resonance frequencies[28] or as a result of parametric resonance.[15] Let the transfer proceed via the level n_{cr}. The principal difference between the models cited in[15,28] and the model considered above is that the population on the level n_{cr} can be much less than unity. Assume that $n_{\text{cr}} \gg 4(f/\alpha)^{2/3}$; then the population on the level n_{cr}, while much less than unity, reaches a maximum if the frequency detuning is $\delta\omega = -\frac{3}{2}\alpha^{1/3}f^{2/3}$.[19,33] It follows therefore that in the models described in[15,29] we can expect the following dependence of $\delta\omega_{\text{opt}}$ on I:

$$\delta\omega_{opt}(I) = -\text{const}\cdot I^{1/3}.$$

3.4. In[6] they discussed the compensation for the anharmonicity by rotation; this compensation takes place if the rotational number j in the initial state is such that

$$|2Bj-\alpha| \ll f. \tag{19}$$

The dissociation probability W will be proportional to the number of molecules satisfying the condition (19). This number is small (since $\alpha \gg f \gg B$); in addition, it depends strongly on the temperature. Using (19), we obtain the expected dependence of W on T:

$$W(T) \sim T^{-1}\exp(-T_m/T), \tag{20}$$

where $T_m = \hbar\alpha^2/4B$. At $\alpha = 7$ cm^{-1} and $B = 0.055$ cm^{-1} we obtain $T_m = 330\,^\circ$K.

According to (12), the maximum value attainable in a time $t_{\text{pulse}} \approx 100$ nsec is $N = 3.1$. If we assume $N = 3$, then $\delta\omega_{\text{opt}} = -\alpha$ and the levels at resonance will be 0–3 (since $E(3) - E(0) = 3\hbar\omega_l$) and the levels 1–2 (in the sense that $E(2) - E(1) = 1\hbar\omega_l$). It was noted in[6] that the probability of dissociation has a maximum as a function of $\delta\omega$ when $\delta\omega = -\alpha$. The single-photon transition 1–2, which takes place for such a detuning without a change of the rotational number, was regarded in[6] as the main cause of the molecule dissociation. It was assumed there that the single-photon transitions 0–1 and 2–3 are a result of cancellation of the anharmonicity by the rotation, i.e., of the change in the rotational number. The coherent three-photon transition 0–3 was not taken into account in[6]. In our opinion, of decisive significance for the dissociation is precisely the transition 0–3, which occurs at the same frequency detuning $\delta\omega = -\alpha$ as the transition 1–2. On the other hand, the influence of the rotation on the dissociation is small if $\delta\omega = \delta\omega_{\text{opt}}$. By measuring the $W(t)$ dependence at $\delta\omega = \delta\omega_{\text{opt}}$, we can choose between the two models (cf. (15) and (20)).

APPENDIX I. DEGENERACY OF QUASISTATIONARY STATES OF A NONLINEAR OSCILLATOR

1. It is known that quasistationary (or quasi-energetic) states of a quantum system situated in the field of an external harmonic force of frequency ω_l is defined as a state whose ψ function takes the form

$$\psi(t, x) = \exp\{-iQt/\hbar\}\psi_0(t, x),$$

where $\psi_0(t, x)$ is periodic in t with a period $2\pi/\omega_l$. The quantity Q is called the quasi-energy and is defined accurate to terms $\hbar\omega_l n$, where n is an integer.

We consider the quasistationary states of a one-dimensional nonlinear oscillator without rotation in the field of laser radiation. We take the Hamiltonian of the system in the form $\hat{H} - E\hat{d}\cos\omega_l t$. Let $E(n)$ and $|n\rangle$ be the eigenvalues and eigenvectors of the operator $\hat{H}$. We assume that at all the values of n of interest to us we have

$$|E(n) - \hbar\omega_l n| \ll \omega_l \tag{21}$$

(we put $E(0) = 0$). We seek the ψ function of the oscillator in the form

$$\psi(t, x) = \sum_m b_m(t)\exp\{-im\omega_l t\}|m\rangle. \tag{22}$$

Let the field E be weak enough, and then the coefficient $b_m(t)$ in the force (21) change little during the time $2\pi/\omega_l$. Substituting (22) in the Schrödinger equation and averaging over the period of the external field, we obtain the system of equations

$$i\hbar\dot{b}_m = (E(m) - \hbar\omega_l m)b_m + V_{mj}b_j, \tag{23}$$

where

$$V_{mj} = -\frac{\hbar f}{2}[(m+1)^{1/2}\delta_{m+1\,j} + m^{1/2}\delta_{m-1\,j}].$$

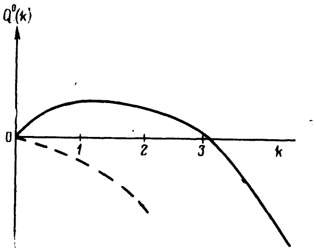

FIG. 2. Plot of Q^0 for $\delta\omega > \alpha/2$ (dashed) and for $\delta\omega < \alpha/2$ (solid). If k is an integer, then $Q^0(k)$ is the quasi-energy. At definite values of $\delta\omega$, the $Q^0(k)$ curve crosses the $Q = 0$ at whole-number points, which means degeneracy of the quasi-energy state.

We note that the nonlinearity in (23) is taken into account only in the form of the $E(n)$ dependence. We introduce the eigenvalues $Q(k)$ and the eigenvectors c_{mk} of Eq. (23): $b_m(t) = \exp\{-iQ(k)t/\hbar\}c_{mk}$ is the solution of (23). It is obvious that $Q(k)$ is the quasi-energy. Let $Q(k)$ pertain to the k-th quasistationary state of the oscillator. If f is so small that the operator V can be neglected, then the solution of (23) is trivial: $c_{mk} = \delta_{mk}$ and

$$Q^0(k) = E(k) - \hbar\omega_l k, \tag{24}$$

where $k = 0, 1, 2, \ldots$ The term $-\hbar\omega_l k$ should be retained, since in our problem there appears in natural fashion a quasi-energy normalization such that as $f \to 0$ the function $Q(k)$ goes over into (24). When $E(n)$ is given by formula (1), we have

$$Q^0(k) = \hbar(\alpha/2 - \delta\omega)k - \hbar\alpha k^2/2.$$

A plot of $Q^0(k)$ as a function of the continuous parameter k is shown in Fig. 2 for $\alpha > 0$ and for different values of $\delta\omega$.

2. It is well known that the perturbing operator $\hat{V}$ influences particularly strongly those eigenvectors of the unperturbed problem which have identical or nearly identical eigenvalues.[43] In our case this means that the influence of $\hat{V}$ on the ground state, which is the state of the oscillator at $t = 0$, will be particularly strong if the quasi-energies are nearly equal, $Q^0(n) \approx Q^0(0)$. We note that the last equality is equivalent to (2).

Let the laser frequency ω_l be close to the resonant value $\omega_l(0; n)$, so that the equality $Q^0(n) = Q^0(0)$ is satisfied with sufficient accuracy. We seek the solution of (23) in the form $b_m(t) = \exp\{-iQt/\hbar\}c_m$. Assuming that the operator $\hat{V}$ is small (more accurately, that $f \ll \alpha$) and using perturbation theory in the Wigner–Brillouin form, it is easy to obtain a system of equations for the coefficients c_0 and c_n:

$$\begin{bmatrix} Q^0(0) + \Delta_{00} - Q, & \Delta_{0n} \\ \Delta_{n0}, & Q^0(n) + \Delta_{nn} - Q \end{bmatrix} \begin{pmatrix} c_0 \\ c_n \end{pmatrix} = 0, \tag{25}$$

where

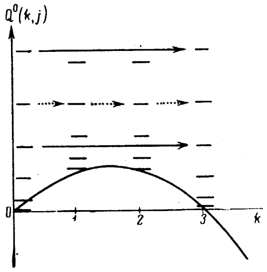

FIG. 3. The quasi-energy terms of the nonlinear oscillator, with allowance for the rotation (the solid curve is a plot of $Q^0(k, j=0)$ against the continuous parameter k). The solid arrow shows the direct transition $0\rightarrow 3$; the three dashed arrows show three successive transitions in the case when the anharmonicity is offset by rotation.

$$\Delta_{0n}=\Delta_{n0}=\frac{V_{01}V_{12}\ldots V_{n-1n}}{(Q^0(1)-Q^0(0))(Q^0(2)-Q^0(0))\ldots(Q^0(n-1)-Q^0(0))}$$
$$=\frac{(-1)^{n-1}}{2}\hbar\alpha\left(\frac{f}{\alpha}\right)^n\frac{n^2}{(n!)^{3/2}}.$$

The coefficients Δ_{00} and Δ_{nn} were calculated in[34]. They are at present of no interest to us, since allowance for them leads only to a small change of the resonant value of the laser frequency $\omega_l(0; n)$. Assuming $\Delta_{00}=\Delta_{nn}=0$, we obtain from (25) two possible values of the quasi-energy $Q(0)$ and $Q(n)$:

$$\left.\begin{matrix}Q(0)\\Q(n)\end{matrix}\right\}=-\frac{\hbar n(\omega_l-\omega_l(0;n))}{2}\pm\left[\frac{\hbar^2n^2(\omega_l-\omega_l(0;n))^2}{4}+|\Delta_{0n}|^2\right]^{1/2}. \tag{26}$$

If the difference that $\omega_l-\omega_l(0;n)$ is large enough, then $Q(0)\approx Q^0(0)$ and $Q(n)\approx Q^0(n)$. At exact resonance $Q(0)=-Q(n)=|\Delta_{0n}|$; the two corresponding solutions of (23) are of the form

$$b_m=\exp\left\{\pm\frac{i|\Delta_{0n}|t}{\hbar}\right\}\frac{\delta_{0m}\pm\delta_{mn}}{\sqrt{2}}. \tag{27}$$

From this we easily obtain formulas (5) and (6).

In[22], the time (5) and the population (6) were not calculated with sufficient consistency, and consequently the analogous formulas do not contain the factor n in front of the expression $\omega_l-\omega_l(0;n)$.

Inclusion of the operator $\hat{V}$ in the n-th order of perturbation theory lifts the degeneracy and leads to repulsion of the quasi-energy terms (see (26)). This is precisely why the coefficients of the expansions of the ground and first quasi-stationary states in $|m\rangle$ take on the form (27). As a result, a population (6) appears on the level n after a time (5).

Figure 3 shows schematically the quasi-energy of different vibrational-rotational states of the oscillator in the zeroth order in f. In the case $\delta\omega=-\alpha$ we have $Q^0(0,j)=Q^0(3,j)$ and $Q^0(1,j')=Q^0(2,j')$. The transitions occur primarily between states with equal Q^0. The direct three-photon transition $0\rightarrow 3$ is possible for all values of j; the transition $0\rightarrow 3$ via three successive single-photon transitions[6] is possible if f satisfies the condition (19); in this case we have

$$Q^0(0,j)\approx Q^0(1,j-1)\approx Q^0(2,j-1)\approx Q^0(3,j).$$

APPENDIX II. ESTIMATE OF THE INFLUENCE OF THE WIDTH OF THE LASER-RADIATION SPECTRUM ON THE EXCITATION OF THE MOLECULE

Let the duration of the laser pulse be t_{pulse}, let t_{cont} be the time necessary to excite the molecule over the quasicontinuum up to dissociation. According to estimates given in[18], t_{cont} can be defined as

$$t_{\text{cont}}\sim\hbar D/(d_{\text{cont}}E)^2; \tag{28}$$

where D is the molecule dissociation energy and d_{cont} is the matrix dipole element for the quasicontinuum: $d_{\text{cont}}\approx(10^{-2}-10^{-3})d_{01}$. If we denote by t_0 the time during which a sufficient population has accumulated on the lower end point of the quasicontinuum for a successive excessive excitation, then obviously in the case of instantaneous dissociation we have

$$t_0+t_{\text{cont}}<t_{\text{pulse}}. \tag{29}$$

Let the spectrum of the laser radiation have a width $\Delta\omega_l$. We can then represent the laser representation in model fashion as a sequence of wave trains with frequency ω_l and duration $t_{\text{coh}}=2\pi/\Delta\omega_l$, which replace one another at the instants

$$t_{\text{coh}},\ 2t_{\text{coh}},\ldots,\ kt_{\text{coh}},\ldots,\ lt_{\text{coh}}\leqslant t_{\text{pulse}}$$

with random variation of the radiation phase θ: $\theta_{k-1}\rightarrow\theta_k$.

Let the oscillator be at the instant $t=kt_{\text{coh}}$ in the quantum state

$$\psi(t=kt_{\text{coh}}-0)=c_0|0\rangle+c_n|n\rangle.$$

It is then necessary to solve the problem of its subsequent motion at $t\geqslant kt_{\text{coh}}$ with new initial conditions

$$\psi(t=kt_{\text{coh}}+0)=c_0|0\rangle+c_n\exp\{in(\theta_k-\theta_{k-1})\}|n\rangle,$$

since the coefficients $b_m=\exp\{-im(\theta+\omega_lt)\}c_m$ remain unchanged when the phase of the field changes rapidly. For the population of the ground level $|0\rangle$ at $(k+1)t_{\text{coh}}\geqslant t\geqslant kt_{\text{coh}}$ we obtain

$$|c_0|^2((k+1)t_{\text{coh}}\geqslant t\geqslant kt_{\text{coh}})=|c_0|^2(t=kt_{\text{coh}})$$
$$\times\cos\left\{\pi\frac{t-kt_{\text{coh}}}{t_{0n}}\right\}+\sin^2\left\{\frac{\pi}{2}\frac{t-kt_{\text{coh}}}{t_{0n}}\right\}$$
$$+\frac{1}{2}i(c_nc_0^*\exp\{in(\theta_k-\theta_{k-1})\}-c_n^*c_0\exp\{-in(\theta_k-\theta_{k-1})\})(t=kt_{\text{coh}})$$
$$\times\sin\left\{\pi\frac{t-kt_{\text{coh}}}{t_{0n}}\right\}. \tag{30}$$

The external force then takes the form

$$E(t)=E\cos(\omega_lt+\theta_k).$$

Since the loss of phase coherence takes place randomly each case, it follows that successive averaging of $|c_0|^2$

from (30) over the change of the phase at the instants $lt_{\text{coh}}, (l-1)t_{\text{coh}}, \ldots, t_{\text{coh}}$ with allowance for the fact that $c_0^2(t=0)=1$ and for the condition (1), yields

$$|\bar{c}_0|^2(t=lt_{\text{coh}})=\left(1+\cos^l\frac{\pi t_{\text{coh}}}{t_{0n}}\right)\Big/2,$$

$$|\bar{c}_n|^2(t=lt_{\text{coh}})=\left(1-\cos^l\frac{\pi t_{\text{coh}}}{t_{0n}}\right)\Big/2.$$

At $t_{\text{coh}} \ll t_{0n}$ we have

$$|\bar{c}_n|^2(t=lt_{\text{coh}}=t_0)=\left[1-\exp\left(-\frac{\pi^2 t_{\text{coh}} t_0}{2t_{0n}^2}\right)\right]\Big/2. \tag{31}$$

We see therefore that the population of the level $|n\rangle$ has a threshold both with respect to time and with respect to field intensity. Namely, a population comparable with unity appears on the n-th level if

$$t_0 \gtrsim t_{0n}^2/t_{\text{coh}}. \tag{32}$$

From (29) and (32) we obtain the necessary condition for the onset of dissociation:

$$t_{0n} \leqslant [t_{\text{coh}}(t_{\text{pulse}}-t_{\text{cont}})]^{1/2}. \tag{33}$$

It is seen from (33), in particular, that near the threshold field intensity, given in accord with (28) by

$$I_{\text{thr}}^{\text{cont}} \sim cD^2/8\pi d_{\text{cont}}^2 t_{\text{pulse}}^2, \tag{34}$$

i.e., at $t_{\text{cont}} \approx t_{\text{pul}}$, the restrictions on t_{0n} are quite stringent.

At intensities not too close to (34), the condition (33) can be rewritten in the form

$$t_{0n} \leqslant (t_{\text{cont}} t_{\text{pulse}})^{1/2}. \tag{35}$$

In particular, it is easy to verify that at an intensity $I \approx 3\times10^7$ W/cm^2 the inequality (35) is satisfied at $n=3$ and is not satisfied if $n>3$.

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1) If the quantities f, E, I, and d are given respectively in units of cm^{-1}, V/cm, W/cm^2, and D = 10^{-18} cgs, then $f = 4.61\cdot10^{-4}\, dI^{1/2} = 1.68\cdot10^{-5}\, Ed$ and $E = 27.5\, I^{1/2}$.

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