[1] C. Cristiansen, Ann. der Physik **19**, 267 (1883).

[2] A. G. Emslie, "Radiation Transfer by Closely Spaced Shields," Aerodynamically Heated Structures, P. E. Glaser, ed. Prentice–Hall, 1962.

[3] SS. M. Rytov, Dokl. Akad. Nauk SSSR **87**, 535 (1952); Teoriya élektricheskikh fluktuatsii i teplovogo izlucheniya (Theory of Electric Fluctuations and Thermal Radiation), AN SSSR, 1953 [Air Force Cambridge Res. Center, 1959, AFCRC-TR-59-1962].

[4] R. P. Caren, J. Heat Transfer, Trans. ASME, Ser. C **94**, 289 (1972).

[5] E. M. Lifshitz, Dokl. Akad. Nauk SSSR **97**, 653 (1954); **100**, 879 (1955); Zh. Eksp. Teor. Fiz. **29**, 94 (1955) [Sov. Phys. JETP **2**, 73 (1956)].

[6] M. L. Levin and S. M. Rytov, Teoriya ravnovesnykh teoplovykh fluktuatsiĭ v élektrodinamike (Theory of Equilibrium Thermal Fluctuations in Electrodynamics), Nauka, 1967.

[7] M. L. Levin and S. M. Rytov, Vetnik MGU, ser. fiz. i. astron. **19**, 165 (1978).

[8] E. G. Cravalho, C. L. Tien, and R. P. Caren, J. Heat Transfer, Trans. ASME, Ser. C **89**, 351 (1967).

[9] G. A. Domoto and C. L. Tien, *ibid.* **92**, 399 (1970).

[10] R. F. Boehm and C. L. Tien, *ibid.* **93**, 405 (1970).

[11] C. Gragstein, Ann. der Physik **7**, 63 (1950).

[12] G. A. Domoto, R. F. Boehm, and C. L. Tien, J. of Heat Transfer, Trans. ASME, Ser. C **92**, 412 (1970).

[13] D. Polder and M. Van Hove, Phys. Rev. **B4**, 3303 (1971).

[14] R. P. Caren, J. Heat Transfer, Trans. ASME Ser. C **94**, 295 (1972).

[15] R. P. Caren, Int. J. Heat Mass Transfer **17**, 755 (1974).

[16] G. A. Grinberg, Izbrannye voprosy matematicheskoĭ teorii élektricheskikh i magnitnykh yavlenii (Selected Problems in Mathematical Theory of Electric and Magnetic Phenomena), AN SSSR, 1948.

[17] M. Born and E. Wolf, Principles of Optics, Pergamon, 1970.

[18] E. M. Lifshitz and L. P. Pitaevskiĭ, Fizicheskaya kinetika (Physical Kinetics), Nauka, 1979.

[19] C. M. Hargreaves, Phys. Lett. **30A**, 491 (1969).

[20] S. S. Kutateladze, N. A. Rubtsov, and Ya. A. Bal'tsevich, Dokl. Akad. Nauk SSSR **241**, 805 (1978) [Sov. Phys. Dokl. **23**, 577 (1978)].

[21] M. A. Miller and V. I. Talanov, Izv. vyssh ucheb. zav. Radiofizika, No. 4, 795 (1961).

Translated by J. G. Adashko

Redistribution of the vibrational energy in the course of laser excitation of high vibrational levels of polyatomic molecules

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(Submitted 26 May 1980)
Zh. Eksp. Teor. Fiz. **79**, 2104–2118 (December 1980)

An analysis is made of a method for calculating the rate coefficients of transitions in a laser field between vicinities of resonances in the band structure of the vibrational quasicontinuum of polyatomic molecules. It is shown that the dependences of the rate coefficients on the molecular energy and on the laser frequency are governed by the type of the strongest anharmonic interaction which locks the excited mode and by the nature of the redistribution of the vibrational energy of the molecules between the degrees of freedom. A study is made of the possibility of using the model of complete stochastization of vibrations in the description of the excitation of a molecule by infrared laser radiation. A model for the increase in the vibrational energy of the directly excited mode is proposed and this model gives the best agreement with the experimental frequency and energy characteristics of the SF$_6$ and SiF$_4$ molecules. The available spectroscopic data on the SF$_6$ molecule are used to find the dependence of the threshold energy of stochastization on the laser interaction frequency.

PACS numbers: 33.80. — b, 33.10.Gx, 33.20.Ea

The process of isotopically selective collisionless infrared dissociation of molecules in a laser field is attracting attention[1-3] and this applies particularly to the nature of the excitation of high vibrational states of polyatomic molecules.[4-9] This includes determination of the characteristics governing the excitation dynamics and of the frequency and energy dependences of the efficiency of the laser interaction, studies of the methods and mechanisms of the redistribution of the vibrational energy of the molecules between the degrees of freedom, etc. In contrast to early studies of the interaction of laser radiation with the vibrational degrees of freedom of molecules,[10,11] recent work on the excitation of polyatomic molecules has led the majority of authors to the conclusion of the need to separate the problem into two parts: spectroscopic and kinetic. The spectroscopic problem involves investigation of the internal interactions and formation of the spectra, whereas the kinetic problem involves the dynamics of excitation of such spectroscopically complex systems.

An approach to the solution of the problem of the excitation of a polyatomic molecule in two stages is suggested in Ref. 6. The first stage is a consideration of the model problem of excitation of a complex multilevel quantum system in a laser field and determination of those characteristics of the spectrum and operator of the interaction with the field which govern the dynamics of the populations. The next stage should be determination of the characteristics of Ref. 6 for real molecules allowing for their specific spectral structure.[12,13] The present paper deals with this second stage.

The problem is as follows. In the case of polyatomic molecules the large number of degrees of freedom causes a rapid rise of the density of vibrational quantum states. Nonlinear anharmonic and Coriolis interactions rapidly induce perturbations of the integrals of motion and loss of the oscillator symmetry, which results in a distribution of the dipole transition cross sections between a large number of levels. The levels of a molecule subjected to a laser field are broadened because of the dynamic Stark effect. The range where the Stark-broadened states begin to overlap is known as the vibrational quasicontinuum. In the region of this quasicontinuum a laser field excites only those levels which lie close to resonances $n\hbar\omega_l$, where ω_l is the frequency of the laser field.[6] The dynamics of the populations in the vicinity of resonances is then given by the rate equations

$$\dot{\rho}_n=-D_n^{n+1}\rho_n-D_n^{n-1}\rho_n+D_{n-1}^{n}\rho_{n-1}+D_{n+1}^{n}\rho_{n+1}. \tag{1}$$

The rate coefficient for a transition from the vicinity of the energy $n\hbar\omega_l$ to the vicinity of the energy $(n+1)\hbar\omega_l$ is equal to the mean-square value of the matrix element of the transition operator between the levels in these vicinities, multiplied by the density of the quantum states in the vicinity of $(n+1)\hbar\omega_l$:

$$D_n^{n+1}=E^2\langle\mu^2\rangle_n^{n+1}g(n\omega_L+\omega_L) \tag{2}$$

$(\hbar\equiv 1)$. The rate coefficient for the reverse transitions is

$$D_{n+1}^{n}=E^2\langle\mu^2\rangle_n^{n+1}g(n\omega_L). \tag{3}$$

The rate coefficients (2) and (3) are those characteristics of a molecule whose calculation makes it possible to determine the dynamics of the level populations.

The idea of describing the process of excitation of polyatomic molecules by the rate equation (1) has been put forward on many occasions.[14-16] However, the rate coefficients have been found phenomenologically and the results obtained have not been in agreement with the experimental results even for two parameters at the same time. For example, the dependence of the energy absorbed by a molecule on the energy of the laser pulses[17,18] required specific phenomenological coefficients, whereas the dispersion characteristic of the quasicontinuum[4,19,20] requires other coefficients. Investigation of the model problems of the excitation of multilevel systems of the planned type[6,7] should make it possible to determine unambiguously the form of the rate coefficients (2) and (3).

Before we calculate the coefficients (2) and (3) on the basis of the spectroscopic data on molecules, it is desirable to point out certain properties of Eq. (1) which facilitate the analysis of the results obtained and simplify their comparison with the experimentally observed dependences and with the theoretical dependences reported elsewhere.[21-23]

It is convenient to rewrite Eq. (1) in the form

$$\frac{\partial}{\partial t}\left(\frac{\rho_n}{g_n}\right)=\frac{D_n^{n+1}+D_n^{n-1}}{2}\left(\frac{\rho_{n+1}}{g_{n+1}}+\frac{\rho_{n-1}}{g_{n-1}}-2\frac{\rho_n}{g_n}\right)+\frac{D_n^{n+1}-D_n^{n-1}}{2}\left(\frac{\rho_{n+1}}{g_{n+1}}-\frac{\rho_{n-1}}{g_{n-1}}\right);\quad g_n\equiv g(n\omega_L). \tag{4}$$

The first term on the right-hand side of Eq. (4) describes spreading of the function $\rho_n g_n^{-1}$, whereas the second term describes its directional motion upward between the energy levels under the action of laser radiation. If

$$(D_n^{n+1}-D_n^{n-1})n\gg D_n^{n+1}+D_n^{n-1},$$

the second term is more important, whereas if

$$(D_n^{n+1}-\overset{(n-1)}{D_n})n\ll D_n^{n+1}+D_n^{n-1},$$

the first term is more important. Therefore, in some cases it is convenient to calculate not the transition probabilities D_n^{n+1} and D_n^{n-1} but the difference between the probabilities of upward and downward transitions, i.e., the probability of acquisition of energy or the coefficient of directional motion of the distribution function

$$Q_n=D_n^{n+1}-D_n^{n-1}.$$

It follows from Eq. (4) that the total energy acquired depends on the laser pulse energy in accordance with a power law if the coefficient Q_n depends on the level number also in accordance with a power law.

We shall derive the formulas for the rate coefficients using the example of excitation of a triply degenerate mode in a molecule of the T_d or O_h symmetry. The structure of the spectrum of triply degenerate modes ν_3 of such molecules has been largely investigated.[12,13,24,25] We shall use the technique of investigating the spectrum and representing its structure developed by Sartakov.[25] The simplest form of the vibrational Hamiltonian of a triply degenerate mode is

$$\hat{H}=\omega_3(a_{3,1}^+a_{3,1}+a_{3,2}^+a_{3,2}+a_{3,3}^+a_{3,3})+\alpha(a_{3,1}^+a_{3,1}a_{3,1}^+a_{3,1}+a_{3,2}^+a_{3,2}a_{3,2}^+a_{3,2}+a_{3,3}^+a_{3,3}a_{3,3}^+a_{3,3})+\beta(a_{3,1}^+a_{3,1}a_{3,2}^+a_{3,2}+a_{3,1}^+a_{3,1}a_{3,3}^+a_{3,3}+a_{3,2}^+a_{3,2}a_{3,3}^+a_{3,3}), \tag{5}$$

where $a_{3,i}^+$ and $a_{3,i}$ are the creation and annihilation operators of the vibrational quanta of the i-th degree of freedom of the mode ν_3.

The eigenvalue spectrum of the operator (5) has a band structure[12]:

$$\mathscr{E}=\omega_3(I_{3,1}+I_{3,2}+I_{3,3})+\alpha(I_{3,1}^2+I_{3,2}^2+I_{3,3}^2)+\beta(I_{3,1}I_{3,2}+I_{3,1}I_{3,3}+I_{3,2}I_{3,3}), \tag{6}$$

where $I_{3,i}$ is the number of quanta in the i-th degree of freedom. We shall consider the levels lying in the vicinity of the energy $\mathscr{E}$ separated by $\varepsilon\ll\omega\ll\mathscr{E}$ from the energy $I_3\omega_3$, where $I_3\equiv I_{3,1}+I_{3,2}+I_{3,3}$. If $I_3\gg 1$, we can regard $I_{3,i}$ as continuous variables. The energy levels in the vicinity of $\mathscr{E}$ have the quantum numbers $|I_{3,1};I_{3,2};I_{3,3}\rangle$, which are located on a circle representing intersection of the plane

$$I_{3,1}+I_{3,2}+I_{3,3}=I_3;\ (I_{3,1};\ I_{3,2};\ I_{3,3})\geqslant 0 \tag{7}$$

and of the second-order surface

$$\varepsilon=\alpha(I_{3,1}^2+I_{3,2}^2+I_{3,3}^2)+\beta(I_{3,1}I_{3,2}+I_{3,1}I_{3,3}+I_{3,2}I_{3,3}). \tag{8}$$

We shall also assume that an external field of intensity E and frequency ω_l interacts only with one of the three degrees of freedom of the mode ν_3, for example, with the first (this assumption does not limit the generality of the treatment). There may be transitions from the vicinity of the energy $\mathscr{E}$ to higher states in the next band, corresponding to an increase in the number of photons in the excited degree of freedom by unity:

$$|I_{3,1};\ I_{3,2};\ I_{3,3}\rangle \to |I_{3,1}+1;\ I_{3,2};\ I_{3,3}\rangle.$$

The frequencies of transitions from states with different quantum numbers are different. The anharmonic frequency shift of a transition is

$$\omega(I_{3,1};\ I_{3,2};\ I_{3,3})-\omega_3=2\alpha I_{3,1}+\beta I_{3,2}+\beta I_{3,3} \tag{9}$$

or, in other words,

$$\omega(I_{3,1};\ I_{3,2};\ I_{3,3})\equiv\partial H/\partial I_{3,1}=\omega_3+2\alpha I_{3,1}+\beta I_{3,2}+\beta I_{3,3}. \tag{10}$$

Using Eqs. (7), (8), and (9), we can obtain the rate coefficients in the classical limit1) $I_{3,1}; I_{3,2}; I_{3,3} \gg 1$:

$$D_I^{I+1}=A^{-1}\int dI_{3,1}dI_{3,2}dI_{3,3}(E\mu_{01})^2 I_{3,1}\delta(\partial H/\partial I_{3,1}-\omega_L)$$
$$\times\delta(I_{3,1}+I_{3,2}+I_{3,3}-I)\delta(I\omega_L-H(I_{3,1};I_{3,2};I_{3,3})), \tag{11}$$

where A is the normalization factor. The physical meaning of Eq. (11) is as follows: the quantity $(E\mu_{01})^2 I_{3,1}$ is the square of the matrix element of the transition operator from the level $|I_{3,1}; I_{3,2}; I_{3,3}\rangle$ to the levels of the next band; $\delta(\partial H/\partial I_{3,1}-\omega_l)$ is the density of the final state in the vicinity of a resonance, so that

$$(E\mu_{01})^2 I_{3,1}\delta(\partial H/\partial I_{3,1}-\omega_L)$$

is the rate coefficient of the transition from the level $|I_{3,1}; I_{3,2}; I_{3,3}\rangle$ in the upward direction. The averaging of this rate coefficient over all the levels which lie in the vicinity of $\mathscr{E}$ and for which the normalized (to unity) distribution function of the quantum numbers f deduced from Eqs. (7) and (8) is

$$f=A^{-1}\delta(I_{3,1}+I_{3,2}+I_{3,3}-I)\delta(I\omega_L-H(I_{3,1};\ I_{3,2};\ I_{3,3})), \tag{12}$$

gives the expression (11).

It is necessary to consider in greater detail the following point. The initial Hamiltonian (5) has the eigenvectors $|I_{3,1}; I_{3,2}; I_{3,3}\rangle$ which are identical with the eigenvectors of the zeroth approximation. Under these conditions the laser field interacting with just one of the degrees of freedom of the excited mode does not affect other degrees of freedom of the same mode and, consequently, averaging of the rate coefficient characterized by the distribution function of the quantum numbers f is, strictly speaking, unjustified. Moreover, the absence of mixing of the quantum states makes invalid the approach based on the solution of model problems,[6] which gives the expressions (2) and (3). However, the occurrence of even a very weak interaction of the type

$$\gamma(a_{3,1}^{+}a_{3,1}^{+}a_{3,2}a_{3,2}+a_{3,2}^{+}a_{3,2}^{+}a_{3,3}a_{3,3}+a_{3,1}^{+}a_{3,1}^{+}a_{3,3}a_{3,3}$$
$$+a_{3,1}a_{3,1}a_{3,2}^{+}a_{3,2}^{+}+a_{3,2}a_{3,2}a_{3,3}^{+}a_{3,3}^{+}+a_{3,1}a_{3,1}a_{3,3}^{+}a_{3,3}^{+}),\quad \gamma\ll\alpha,\beta, \tag{13}$$

which is again allowed by the symmetry,[25] alters considerably the pattern. It mixes the levels which are in the vicinity of a given energy and, consequently, justifies averaging with the aid of the distribution function f of Eq. (12) and the use of the model approach of Ref. 6. Mixing of the levels in the upper band ensures the distribution of the transition cross sections $|I_{3,1}; I_{3,2}; I_{3,3}\rangle \to |I_{3,1}+1; I_{3,2}; I_{3,3}\rangle$ between a large number of levels located near $|I_{3,1}+1; I_{3,2}; I_{3,3}\rangle$ and justifies the use of the expression

$$(E\mu_{01})^2 I_{3,1}\delta(\partial H/\partial I_{3,1}-\omega_L)$$

as the rate coefficient of transitions from the level $|I_{3,1}; I_{3,2}; I_{3,3}\rangle$. In its turn, mixing of the levels in the lower band allows us to average the rate coefficients of the upward transition over all the levels from the vicinity of a given energy.

The same results are obtained for any other weak interaction that ensure mixing of the nearby quantum states. On the other hand, such a weak interaction does not alter significantly the rate coefficients of Eq. (11) which are unaffected by the selection of the basis.

A calculation of Eq. (11) subject to allowance for Eqs. (5) and (9) and normalization of the function (12) gives the expression

$$D_I^{I+1}=\frac{(E\mu_{01})^2(\Delta'-I)}{\beta-\alpha}\Theta(I-\Delta')\Theta(\Delta')\Theta(\varepsilon'-\Delta'^2+I\Delta')$$
$$\times(4\varepsilon'+4\Delta'I-3\Delta'^2)^{-1/2}\left[1-\frac{3}{\pi}\arccos\left(4-\frac{12\varepsilon'}{I^2}\right)\Theta(I^2-4\varepsilon')\right]^{-1}, \tag{14}$$

where $\Theta(x)$ is the Heaviside theta function and

$$\Delta'=(\Delta-\alpha I)(\beta-\alpha)^{-1},\ \varepsilon'=(\varepsilon-\alpha I^2)(\beta-2\alpha)^{-1},\ \Delta=\omega_3-\omega_L.$$

The coefficient Q_I, i.e., the difference between the rate coefficients of the upward and downward transitions, can be calculated—within the framework of the assumptions made here—employing a formula similar to Eq. (11):

$$Q_I=A^{-1}\int dI_{3,1}dI_{3,2}dI_{3,3}(E\mu_{01})^2\delta(\partial H/\partial I_{3,1}-\omega_L)\delta(I_{3,1}$$
$$+I_{3,2}+I_{3,3}-I)\delta(I\omega_L-H(I_{3,1};I_{3,2};I_{3,3})). \tag{15}$$

The above approach and the main features of the calculation of the rate coefficients were tested by us by application to a triply degenerate mode. There were two important features of this calculation. Firstly, the rate coefficient of upward transitions from the $|\{I\}\rangle$ level with quantum numbers $\{I\}$ is governed by the quantity $(E\mu_{01})^2 I_1\delta(\omega_l-\partial H/\partial I_1)$, which is the product of the square of the matrix element of the transition and the density of the final quantum states. To obtain this expression it is sufficient to allow only for the strongest anharmonic interaction with the maximum value $\partial H_{\text{anh}}/\partial I_1$. Interactions of higher orders or simply weaker interactions make no direct contribution to the results. However, their contribution appears indirectly via the form of the distribution function of the quantum numbers f. The use of the distribution function f (taking into account generally not only the energy but also the phase ϑ of the vibrations) is another important feature of the approach. The point is this: when molecules are excited with laser radiation far from all the quantum states (even those which are in resonance) are capable of participating in the same way in the energy acquisition process, i.e., the excitation process does not apply everywhere throughout the phase space of the molecule. In the example given above the distribution function of the quantum numbers f is given by Eq. (12). It is assumed that the excitation process involves only levels of one mode and only those which are in the vicinity of the energy $\mathscr{E}=I\omega_l$ and correspond to a fixed total number of photons in a mode at a fixed energy.

In general, the classical expression for the rate coefficients is written in the form

$$D_I^{I+1}=(E\mu_{01})^2\int I_1\delta\left(\omega-\frac{\partial H}{\partial I_1}\right)f(\{I\};\{\vartheta\})d^nId^n\vartheta. \tag{16}$$

The above equation is the classical limit for the more general expression

$$D(\mathscr{E};\mathscr{E}')=\bar{g}(\mathscr{E}')E^2\langle\mathrm{Tr}(\delta(\mathscr{E}-\hat{H})\hat{\mu}^+\delta(\mathscr{E}'-\hat{H})\hat{\mu}^-)\rangle,$$
$$\mathscr{E}'\in(\mathscr{E}'+a;\mathscr{E}'-a),\ \mathscr{E}\in(\mathscr{E}+a;\mathscr{E}-a),\ a\to0,$$

where Tr represents the trace operation only between the levels which are populated significantly in the process of energy acquisition and $\bar{g}$ is the density of these levels. In the classical limit, we have to make the substitution

$$\bar{g}\,\mathrm{Tr}\to\int d^nId^n\vartheta f(\{I\};\{\vartheta\})\ldots$$

and ignore the noncommutative nature of the operators $\hat{\mu}^\pm$ and $\hat{H}$. For this reason the terms corresponding to laser excitation of hybrid vibrations disappear. Such corrections can be allowed for separately.

Before calculating the rate coefficients in accordance with Eq. (16), it is necessary to consider in greater detail a possible structure of the function f. Strictly speaking, in the vicinity of each energy there is a distribution function which is the result of numerous although relatively weak anharmonic interactions. Situations are possible when the ergodic hypothesis is valid, i.e., when anharmonic interactions of higher orders mix all the levels lying in the vicinity of a given energy and the excitation process extends over the whole phase volume of the δ-like energy layer. In this case, we have

$$f=\delta(\mathscr{E}-H(\{I\};\{\vartheta\}))A^{-1}. \tag{17}$$

There is also a possible situation in which the ergodic hypothesis is known to be invalid. In classical mechanics the inapplicability of the ergodic hypothesis is ensured by the Kolmogorov criterion[26]

$$\left|m\frac{\partial H}{\partial I_i}-p\frac{\partial H}{\partial I_k}\right|\gg V_{mp} \tag{18}$$

for any value of m and p, where the matrix element V_{mp} is defined as

$$V_{mp}=\int d^n\vartheta V(\{I\};\{\vartheta\})\exp(im\vartheta_i-ip\vartheta_k).$$

In more general cases of non-Hamiltonian or nonstationary mechanics the situation is much more complex,[27] but even then there are stochasticity criteria. The questions on what happens when the condition (18) is not obeyed and to what extent it is possible to use the ergodic hypothesis are dealt with in a number of papers (see, for example, Refs. 28 and 29).

In investigations of the interaction of laser radiation with polyatomic molecules it is essential to use a quantum analog of the Kolmogorov criterion (18). There is no conflict between the use of the classical expression for the rate coefficients (16) and an allowance for quantum effects in the criterion (18). In fact, the nature of the rate coefficient itself creates a very strong anharmonic interaction, the changes in the energies during transitions are large, and the quantum corrections to the transition cross sections are small: at the same time, the interaction governing the function f is weak, the density of levels is high, and the role of the quantum corrections is considerable.

It is usual to assume[28,29] that reversal of the inequality (18) not only permits ergodicity but also establishes it. Generalization of this conclusion to the quantum range can be represented in the form

$$|E_a-E_b|\ll G_{ab}, \tag{19}$$

in other words, the difference between the energies of levels $|a\rangle$ and $|b\rangle$ should be less than the matrix element G_{ab} of the transition between them due to the anharmonic perturbation $\hat{V}$ and the matrix element of the transition operator considered in the quantum case should allow for all orders of perturbation theory:

$$G_{ab}=\langle a|\hat{V}|b\rangle+\sum_c\langle a|\hat{V}|c\rangle(E_a-E_c)^{-1}\langle c|\hat{V}|b\rangle+\ldots. \tag{20}$$

It is very inconvenient to use the criterion (19) together with the expression (20) because of the need to know the actual values of E_a, E_b, and G_{ab}. It is more convenient to employ a different criterion obtained by averaging (19) over the final states:

$$\langle(G_{ab})^2\rangle_b g_b^2\gg1, \tag{21}$$

where g_b is the density of the final states. In other words, ergodization occurs if the mean-square matrix element of the transition exceeds the characteristic separation between the levels of the final states. By replacing the criterion (19) with the criterion (21), we are in fact assuming the absence of any relationships which would result in unavoidable appearance of a large number of terms with small denominators from the series (20), i.e., we are postulating comparability of the contributions of all the anharmonic corrections of the same order to the expression (20), which implies an approximate equivalence of all the state decay channels.

The opposite situation when a specific decay channel is preferred is not exceptional: it occurs, for example, in the case of the SF_6 molecule. Although the existence of a preferential decay channel does not alter significantly the nature of the interaction of the distant levels, the change in the interaction of states which are close in the phase space is considerable. This situation will be discussed in detail later. Here, we shall use the criterion (21) to estimate the ranges of the parameters of the molecules within which stochastization of the vibrations occurs in the absence of favorable decay channels.

For convenience, we shall introduce a parameter λ representing the average anharmonic interaction. The K-th order anharmonic interaction corresponds to $\lambda^{K/2}$. We shall regard the criterion (21) for the anharmonic interaction to be of the order of $2s$, which corresponds to a total change in the quantum numbers by $2s$. The density of such states is

$$g\approx C_{d+s}^{d-1},$$

where d is the number of degrees of freedom.

The square of the matrix element of a transition depends on the energy distribution between the degrees of freedom corresponding to the investigated state. If decay of a localized state is considered, there are states in which all the vibrational energy $n\omega$ is concentrated in one degree of freedom so that the matrix element of the transition is

$$G^2(s)\approx\lambda^{2s}n^s;\qquad g\approx\frac{(d+s)!}{(d-1)!(s+1)!}.$$

In the case of a delocalized state, i.e., a state corresponding to a uniform energy distribution between all the degrees of freedom, the matrix element is

$$G^2(s)\approx\lambda^{2s}\left(\frac{n}{d}\right)^{2s};\qquad g\approx2^d\left[\frac{(s+d/2+1)!}{s!(d/2+1)!}\right]^2.$$

For these matrix elements the criterion (21) can be satisfied for

$$\begin{aligned}&n>4/\lambda d,\quad \text{if}\quad n\gg d;\ \lambda^{1/2}d\ll2,\\&\qquad\text{for any } n,\ \text{if}\ \lambda^{1/2}d>2\end{aligned}\tag{22}$$

in the case of initially delocalized states and when

$$n>1/\lambda^2d^2\ \left(\text{ if }\quad \lambda d>1,\ \text{then } n \text{ can have any value}\right),\tag{23}$$

if the initial states are localized. This means that the stochastic behavior can be observed for $n>4/\lambda d$, and complete stochastization (i.e., ergodicity or complete absence of localized states) occurs for $n>1/\lambda^2d^2$. However, in the case of molecules with a large number of degrees of freedom d, $d\gg\lambda^{-1}$, a complete stochastization is observed for any value of n, i.e., beginning from the first term.

The case of complete stochastization corresponds to the following ergodic distribution function

$$f=A^{-1}\delta(\mathscr{E}_1+\mathscr{E}_2+\ldots+\mathscr{E}_d-\mathscr{E})\approx\prod_{p=1}^{d}\exp\left(-\frac{\mathscr{E}_p}{\langle\mathscr{E}\rangle}\right)A^{-1},\quad\langle\mathscr{E}\rangle\equiv T=\mathscr{E}/d.\tag{24}$$

Localized states exist above the stochastization limit if $4\lambda d<1$ or $d<1/4\lambda$.

A typical number of quanta s transferred from one mode to another in one event (i.e., the characteristic change in the vibrational quantum numbers) is as follows: in the case of localized states

$$s\approx\begin{cases}n, & n\ll d\\ d\lambda n^{1/2}, & n\gg d\end{cases},\tag{25a}$$

in the case of delocalized states

$$s\approx\begin{cases}(\lambda nd/4)^{1/2}, & n\gg d\\ (\lambda d^2/4)^{1/2}, & n\ll d\end{cases},\tag{25b}$$

and the probability of such transitions

$$W=\sum_s G^2(s)g(s)$$

[the sum is taken over those values of s for which $G^2(s)g^2(s)>1$] has the following value for localized states

$$W\propto\omega^*(1+\lambda^2d)^n,\tag{26a}$$

whereas in the case of delocalized states, we have

$$W\propto\omega^*e^{\lambda n},\tag{26b}$$

where ω^* is the characteristic vibrational frequency.

The order of magnitude of the quantity λ can be estimated from

$$\lambda\sim\eta^2\sim\left(\frac{m_e}{M}\right)^{1/2},\quad\eta=\left(\frac{m_e}{M}\right)^{1/4},$$

where η is the Born–Oppenheimer parameter. Typically in the case of molecules we have $\lambda\approx1/30-1/200$. Consequently, the characteristic (number of dimensions of a system in which localized states can be observed above the stochastization threshold is $d<50$. Molecules with this number of degrees of freedom are precisely those which can be regarded as promising from the point of view of laser photochemistry. Laser excitation of localized states above the stochastization threshold may ensure preferential occurrence of a chemical reaction in a nontrivial channel.

There have been reports[30] according to which the ergodic hypothesis gives results in good agreement with the experimental data for molecules which have $d>100$ degrees of freedom. According to the above estimates, the motion of a molecule with such a large number of degrees of freedom becomes stochastic beginning right from the first level.

The above considerations ignore the possibility of the occurrence of vibrational Fermi resonances in molecules which can ensure specific preferential molecule decay channels. An allowance for this factor requires knowledge of the vibrational spectrum and of the anharmonic interaction constants. The most thoroughly investigated case is that of the SF_6 molecule. The large (but still incomplete) amount of spectroscopic data on this molecule makes it possible to estimate the critical energy above which the decay of states of an excited mode to the nearest hybrid states becomes significant. In the case of the SF_6 molecule the frequency of the infrared-active laser-excited mode $\nu_3=948$ cm^{-1} is closest to the frequencies of the hybrids $\nu_2+\nu_6=973$ cm^{-1} and $3\nu_6=1030$ cm^{-1}, and to the vibration $\nu_2+\nu_4$ (Ref. 31). The transfer of excitation to these hybrid vibrations corresponds to minimal denominators in Eq. (20). However, the transfer of excitation from the ν_3 mode to the hybrid $\nu_2+\nu_4$ cannot occur because of the absence (for symmetry reasons) of the anharmonic interaction constant. The constant governing the transfer of excitation from the ν_3 to the $3\nu_6$ mode is approximately 2.5×10^{-2} cm^{-1} and for the $\nu_3\to\nu_2+\nu_6$ channel this constant is $\Lambda_{236}\approx2.4$ cm^{-1}. It is this last channel that governs the critical energy of the SF_6 molecule.

The anharmonic correction to the Hamiltonian resulting in the transfer of excitation from ν_3 to $\nu_2+\nu_6$ is

$$\begin{aligned}H_{236}=\Lambda_{236}[&3Q_a(E_g)(\dot{Q}_b\dot{Q}_{2b}-\dot{Q}_a\dot{Q}_{2a})\\&+Q_b(E_g)(2\dot{Q}_c\dot{Q}_{2c}-\dot{Q}_a\dot{Q}_{2a}-\dot{Q}_b\dot{Q}_{2b}],\end{aligned}\tag{27}$$

where $Q_{a,b}(E_g)$ are the coordinates of ν_2; $Q_{a,b,c}$ are the coordinates of ν_6; $Q_{2a,2b,2c}$ are the coordinates of ν_3. Moreover, we have to allow for the anharmonic interaction of fourth order which results in mutual changes in the frequencies of the ν_3, ν_2, and ν_6 modes:

$$\begin{aligned}H_{3326}=&\varkappa_{36}(Q_a{}^2+Q_b{}^2+Q_c{}^2)(Q_{2a}{}^2+Q_{2b}{}^2+Q_{2c}{}^2)\\&+\lambda_{36}(Q_a{}^2Q_{2a}{}^2+Q_b{}^2Q_{2b}{}^2+Q_c{}^2Q_{2c}{}^2)+\eta_{36}(Q_bQ_cQ_{2b}Q_{2c}\\&+Q_aQ_cQ_{2a}Q_{2c}+Q_aQ_bQ_{2a}Q_{2b})+\varkappa_{32}(Q_a{}^2(E_g)\\&+Q_b{}^2(E_g))(Q_{2a}{}^2+Q_{2b}{}^2+Q_{2c}{}^2)+\lambda_{23}[(Q_b{}^2(E_g)-Q_a{}^2(E_g))(2Q_{2b}{}^2-Q_{2a}{}^2\\&-Q_{2c}{}^2)+Q_a(E_g)Q_b(E_g)(Q_{2a}{}^2-Q_{2c}{}^2)].\end{aligned}\tag{28}$$

McDowell *et al.*[32] determined experimentally the constants $\varkappa_{36} = -2\ \text{cm}^{-1}$ and $\varkappa_{32} = -1\ \text{cm}^{-1}$. There are no published values of the constants λ_{36}, η_{36}, or λ_{23}. We shall assume that they are small and ignore them in a subsequent discussion.

The effective transfer of excitation requires that the condition of resonance between vibrations of the excited mode and the nearest hybrid be satisfied:

$$\begin{aligned}&\omega_3 I_3+\alpha I_3^2+(\beta-2\alpha)(I_{3,1}I_{3,2}+I_{3,1}I_{3,3}+I_{3,2}I_{3,3})\\&=\omega_3(I_3-1)+\omega_2+\omega_6+(I_3-1)(\varkappa_{2,3}-\varkappa_{3,6})+\alpha(I_3-1)^2\\&\quad+(\beta-2\alpha)(I_{3,1}I_{3,2}+I_{3,1}I_{3,3}+I_{3,2}I_{3,3}-I_{3,2}-I_{3,3}),\end{aligned} \tag{29}$$

where α, β, and $I_{3,i}$ are defined in the same ways as in Eq. (6). Equation (29) is obtained on the assumption of decay of a quantum corresponding to a vibration of the first degree of freedom of the mode ν_3 and amounting to $-I_{3,1}$. It follows from Eq. (29) that

$$I_{3,1}=\frac{(\beta-\varkappa_{2,3}-\varkappa_{3,6})I_3-(\omega_2+\omega_6-\omega_3)}{\beta-2\alpha}. \tag{30}$$

We shall find the dependence of the minimum detuning from the harmonic position of the energy $\varepsilon_{\min}(I_3)$ as a function of the number of quanta I_3 in the mode ν_3, since the decay of the mode ν_3 occurs in the vicinity of this energy. Using Eqs. (29) and (30) and the relationship between the arithmetic and geometric means, we obtain

$$\begin{aligned}\varepsilon_{\min}(I_3)=&\left[\alpha+\frac{(\varkappa-2\alpha)(\beta-{}^1/_2\alpha+{}^3/_4\varkappa)}{\beta-2\alpha}\right]I_3^2\\&+\frac{\beta-{}^3/_2\varkappa+\alpha}{\beta-2\alpha}(\omega_2+\omega_6-\omega_3)I_3-\frac{3(\omega_2+\omega_6-\omega_3)^2}{4(\beta-2\alpha)},\end{aligned} \tag{31}$$

where $\varkappa = \varkappa_{32} + \varkappa_{36}$. This dependence is plotted in Fig. 1, which shows that the critical energy depends on the interaction frequency. This energy increases as a result of a shift of the interaction energy toward the red end.

The existence of a leading decay channel alters also the nature of the distribution of the molecular energy between the degrees of freedom. A hybrid vibration becomes detuned from resonance and the process of successive energy transfer ceases as soon as the number of quanta in the mode ν_3 becomes less than the critical value. If this situation occurs below the threshold of complete stochastization of Eq. (22), which may generally lie above the minimum dissociation limit, the distribution function becomes strongly nonequilibrium.

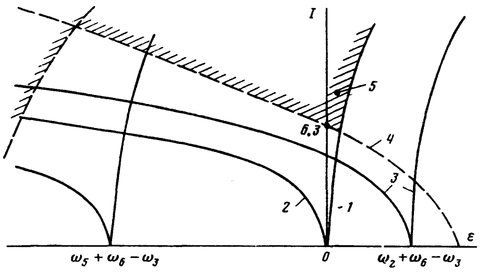

FIG. 1. 1) Blue boundary of the zone of the ν_3 mode. 2) Red boundary of the zone of the ν_3 mode. 3) Boundary of the zone of hybrid vibrations $n\nu_3+\nu_2+\nu_6$. 4) Boundary of $\nu_3\to\nu_2+\nu_6$ decay. 5) Stochastization region where $\nu_2+\nu_6$ states are mixed with ν_3. In the case of the SF_6 molecule at the frequency of the main transition of the ν_3 mode the stochastization region begins from an energy of the order of 7 quanta of ν_3. The red boundary of the zone of the ν_3 mode shifts faster than the boundary of the $\nu_3\to\nu_2+\nu_6$ decay and, therefore, excitation at frequencies strongly shifted in the direction of the red edge under conditions of two-frequency laser interaction may occur within the limits of one mode until a second decay channel is activated.

It is convenient to use in this case the model of "divergence" of the vibrational energy of the mode excited directly by laser radiation. This model presupposes that only the states having at least a critical number of quanta in the excited mode can be mixed and the energy concentrated in this mode E_c is higher than the average energy in each of the other degrees of freedom. The main contribution to the expression for the rate coefficients is made by the statistically preferred states, which correspond to the minimum possible energy E_c in the excited mode. The model of divergence of the vibrational energy is characterized by its own distribution function f:

$$f=A^{-1}\delta(\omega_3 I_{3,1}+\omega_3 I_{3,2}+\omega_3 I_{3,3}-E_c). \tag{32}$$

This divergence model applies not only to the SF_6 molecule but also to a number of highly symmetric polyatomic molecules in which leading decay channels are very probable. For example, in the case of the SiF_4 molecule there are grounds for expecting the existence of a critical energy representing approximately 14 quanta of the main transition in the ν_3 band.

We shall now give the results of calculations of the rate coefficients made using Eq. (16) and the distribution functions (24) and (32). The case of complete localization of the excitation in a triply degenerate mode is considered above [Eqs. (14) and (15)]. We shall also discuss various forms of the strongest anharmonic interactions:

$$H_{\text{anh}}=\gamma I_1^{1/2}I_2\cos(\vartheta_1-2\vartheta_2),\qquad \omega_1=2\omega_2 \tag{33}$$

$$H_{\text{anh}}=\gamma I_1^{1/2}I_2^{1/2}I_3^{1/2}\cos(\vartheta_1-\vartheta_2-\vartheta_3),\qquad \omega_1=\omega_2+\omega_3, \tag{34}$$

$$H_{\text{anh}}=\alpha(I_{3,1}^2+I_{3,2}+I_{3,3})+\beta(I_{3,1}I_{3,2}+I_{3,1}I_{3,3}+I_{3,2}I_{3,3}), \tag{35}$$

$$H_{\text{anh}}=\zeta BJI_1^{1/2}I_2^{1/2}\sin(\vartheta_1-\vartheta_2),\quad \omega_1=\omega_2. \tag{36}$$

The rate coefficients Q and D for the Hamiltonian (33) and the distribution function (24) can be expressed in terms of the Whittaker function:

$$\begin{aligned}D(T,\Delta)&=\frac{TE^2\mu^2}{2\pi\omega_1\Delta}\Gamma\left(\frac{5}{2}\right)\Gamma\left(-\frac{3}{2}\right)\exp\left(\frac{\omega_1\Delta^2}{8T\gamma^2}\right)W_{-2,0}\left(\frac{\omega_1\Delta^2}{4T\gamma^2}\right),\\Q(T,\Delta)&=\left|\frac{T\gamma}{2\omega\Delta}\right|E^2\mu^2\exp\frac{\omega_1\Delta^2}{T\gamma^2}W_{-1,0}\left(\frac{2\omega_1\Delta^2}{T\gamma^2}\right)\end{aligned} \tag{37}$$

on condition that $\Delta/\gamma \gg 1$ or $T/\omega \gg 1$. Here, $\Delta = \omega_1 - \omega_l$; $T \equiv \langle \mathscr{E} = n\omega_1/d$ is the average energy in one degree of freedom. In the case of high values of $\omega_1\Delta^2/T\gamma^2 \gg 1$, Eq. (37) reduces to

$$Q\approx\frac{T^2\gamma^3}{4\omega_1^2|\Delta|^3}\frac{(E\mu)^2}{|\Delta|}\sim\frac{1}{|\Delta|^4},\qquad D\sim\frac{1}{|\Delta|^5}. \tag{38}$$

For the Hamiltonian (34) and the distribution function (24), we have

$$\begin{aligned}Q(T,\Delta)&=\frac{E^2\mu^2(\omega_2\omega_3)^{1/2}}{\gamma(2T\omega_1)^{1/2}}\exp\left(\frac{\omega_2\omega_3\Delta^2}{8T\omega_1\gamma^2}\right)D_{-3}\left(\left(\frac{\omega_3\omega_2\Delta^2}{2T\omega_1\gamma^2}\right)^{1/2}\right)\\D(T,\Delta)&=\frac{E^2\mu^2(T\omega_2\omega_3)^{1/2}}{\gamma\omega_1^{3/2}}3\sqrt{2}\exp\left(\frac{\omega_2\omega_3\Delta^2}{8T\omega_1\gamma^2}\right)D_{-5}\left(\left(\frac{\omega_3\omega_2\Delta^2}{2T\omega_1\gamma^2}\right)^{1/2}\right),\end{aligned} \tag{39}$$

where D_i is the parabolic cylindrical function. The asymptotic behavior in the limit $\omega_2\omega_3\Delta^2/2T\omega_1\gamma^2 \gg 1$ is as follows:

$$Q=\frac{E^2\mu^2(\omega_1\omega_2)^{1/2}}{\gamma(2T\omega_1)^{1/2}}\left(\frac{\omega_2\omega_3\Delta^2}{2T\omega_1\gamma^2}\right)^{-1/2},\quad D=3\frac{E^2\mu^2(T\omega_2\omega_3)^{1/2}}{\gamma\omega_1^{3/2}}\left(\frac{\omega_2\omega_3\Delta^2}{2T\omega_1\gamma^2}\right)^{-5/2}. \tag{40}$$

For the Hamiltonian (36) and the distribution function (24), we have

$$Q=\frac{1}{2\pi}\frac{2E^2\mu^2}{B\zeta J}\left(1+\frac{4\Delta^2}{B^2\zeta^2J^2}\right)^{-3/2},\quad D=\frac{2T}{4\pi\omega}\frac{2E^2\mu^2}{B\zeta J}\left(1+\frac{4\Delta^2}{B^2\zeta^2J^2}\right)^{-5/2}. \tag{41}$$

For the Hamiltonian (35) and the distribution function (24), we obtain

$$D=\frac{2e^{-\omega\Delta/T\beta}}{\beta^2}\left[\frac{\omega}{T}\left(1-\frac{2\alpha}{\beta}\right)\right]^{-2}\left[\frac{\Delta\omega}{T}\left(1-\frac{2\alpha}{\beta}\right)-4\alpha\right],\quad Q=\frac{2e^{-\omega\Delta/T\beta}}{\beta^2}\left[\frac{\omega}{T}\left(1-\frac{2\alpha}{\beta}\right)\right]^{-3}\left[\frac{\Delta\omega}{T}\left(1-\frac{2\alpha}{\beta}\right)-2\alpha\right]. \tag{42}$$

For the Hamiltonian (35) and the distribution function (32) (corresponding to the model of divergence of the vibrational energy on the assumption that the critical energy depends weakly on the frequency), we obtain

$$D=2\left(\frac{E_c}{\omega}-\frac{\Delta\omega-\beta E_c}{\omega(2\alpha-\beta)}\right)\left(\frac{\Delta\omega-\beta E_c}{\omega(2\alpha-\beta)}\right)\Theta\left(\frac{E_c}{\omega}-\frac{\Delta\omega-\beta E_c}{\omega(2\alpha-\beta)}\right)\times\Theta\left(\frac{\Delta\omega-\beta E_c}{\omega(2\alpha-\beta)}\right)\frac{E^2\mu^2}{\beta},$$
$$Q=\frac{E^2\mu^2}{\beta}2\left(\frac{E_c}{\omega}-\frac{\Delta\omega-\beta E_c}{(2\alpha-\beta)\omega}\right)\Theta\left(\frac{E_c}{\omega}-\frac{\Delta\omega-\beta E_c}{\omega(2\alpha-\beta)}\right)\Theta\left(\frac{\omega\Delta-\beta E_c}{\omega(2\alpha-\beta)}\right), \tag{43}$$

in which case the rate coefficients are independent of n.

We can thus see that in a fairly general situation we can describe the dynamics of excitation of the vibrational quasicontinuum of polyatomic molecules provided we use[2)] the rate equation (4) and the rate coefficients (16). It seems that a good agreement between calculations and experiment requires a numerical solution of Eq. (4) with the rate coefficients of Eq. (16) for various values of the energy in a pulse and various excitation frequencies. However, even a qualitative analysis of the solutions of Eq. (4) with the rate coefficients (15) and (37)–(43), made by one of the present authors,[34] has shown that in a series of symmetric polyatomic molecules of the SF_6 or SiF_4 type the best agreement with experiment is given by the model of divergence of the vibrational energy of the mode excited directly.

In fact, it follows from Eq. (4) that the total energy acquired by a molecule $\omega\langle n\rangle \equiv dT \equiv d\langle\mathscr{E}\rangle$ in a time t is governed by the nature of the coefficient Q

$$\langle\dot{\mathscr{E}}\rangle=\omega Q(\langle\mathscr{E}\rangle). \tag{44}$$

If $Q \propto \mathscr{E}\rangle^{\alpha}$, the total energy acquired in this way is proportional to the energy of a laser pulse taken to the power $(1-\alpha)^{-1}$,

$$\langle\mathscr{E}\rangle\propto[(1-\alpha)\mathscr{E}_I]^{1/(1-\alpha)};$$

if $\alpha=1$, the dependence is exponential. If Q is independent of $\langle\mathscr{E}\rangle$, as is true in the model of divergence of the vibrational energy or in some special case of the model of localization of the excitation energy in one mode, the energy acquired by a molecule is a linear function of the laser pulse energy.

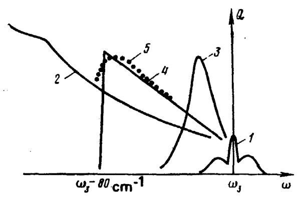

FIG. 2. 1) Line absorption spectrum of the SiF_4 molecule. 2) Frequency dependence of the coefficient Q of Eq. (15) for high vibrational states on the assumption of excitation of just one mode. 3) Frequency dependence of Q on the assumption of complete stochastization [Eq. (42)]. 4) Frequency dependence of Q in the divergence model [Eq. (43)], E_c= 14 quanta. 5) Experimental dependence of the effectiveness of excitation of the SiF_4 molecule on the frequency of the second step under conditions of two-frequency laser interaction.

On the other hand, the experimentally observed considerable width of the frequency characteristic of the effectiveness of the excitation of the SF_6 and SiF_4 molecules under conditions of two-frequency laser interaction[4,20] clearly exclude the possibility of applying the model of complete stochastization in describing the process of energy acquisition by these molecules in a laser field, since this model gives rise to narrow frequency characteristics given by Eq. (42). In the case of the SiF_4 molecule the best agreement with the experimental results is given by the divergence model and the critical energy is 14 quanta (see Fig. 2).

We shall now formulate the main conclusions of the present investigation.

1. The rate equations of transitions between immediate vicinities of resonances in the band structure of the quasicontinuum is governed by the nature of the strongest anharmonic interaction involving the mode excited by infrared radiation and by the nature of the distribution of the vibrational energy of the molecule between the degrees of freedom.

2. The anharmonic or Coriolis interaction in the s-th order of perturbation theory may cause decay of states (stochastization of vibrations) if the product of the density of the states interacting in this order and the mean-square element of the interaction exceeds unity.

3. In the case of polyatomic molecules with not too many atoms there may be a situation when the states corresponding to energy localization in one vibrational mode become stochastic later than the states corresponding to a uniform distribution of the energy between the degrees of freedom. In this case it is very likely that the decay of localized states is due to the presence of a leading decay channel, which results in mixing of the states containing at least n_{cr} quanta in the directly excited mode (divergence model).

4. The model of divergence of the vibrational energy of the directly excited mode ensures, in contrast to the other models, a satisfactory agreement with the experimental results for the SiF_4 molecule (as well as for the SF_6 molecule) simultaneously in respect of two independent characteristics: frequency and energy.

5. The critical energy may depend on the frequency

of the interaction. For example, in the case of the SF_6 molecule and one-frequency interaction at the frequency of the main transition, the available experimental data on the anharmonic constants gives an estimate of the critical energy which amounts to 7 quanta.

1) The expression (11) remains valid also in the quantum case if we replace integration with summation and the δ function with the Kronecker symbol.

2) Another form of the rate coefficients is suggested by Bagratashvili *et al.*[33] For the CF_3I molecule on the assumption that the characteristic anharmonic interaction is higher than the density of resonances of the vibration frequencies.

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[1] N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, Can. J. Phys. **51**, 1281 (1973).

[2] R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 597 (1974) [JETP Lett. **20**, 273 (1974)].

[3] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and L. A. Shelepin, Zh. Eksp. Teor. Fiz. **69**, 836 (1975) [Sov. Phys. JETP **42**, 427 (1975)].

[4] N. V. Karlov and S. S. Alimpiev, Izv. Akad. Nauk SSSR Ser. Fiz. **43**, 366 (1979).

[5] R. V. Ambartsumyan, Yu. A. Gorokhov, G. N. Makarov, A. A. Puretskiĭ, and N. P. Furzikov, Kvantovaya Elektron. (Moscow) **4**, 1590 (1977) [Sov. J. Quantum Electron. **7**, 904 (1977)].

[6] V. M. Akulin and A. M. Dykhne, Zh. Eksp. Teor. Fiz. **73**, 2098 (1977) [Sov. Phys. JETP **46**, 1099 (1977)].

[7] A. A. Makarov, V. T. Platonenko, and V. V. Tyakht, Zh. Eksp. Teor. Fiz. **75**, 2075 (1978) [Sov. Phys. JETP **48**, 1044 (1978)].

[8] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and B. G. Sartakov, O mekhanizme vozbuzhdeniya vysokikh kolebatel'nykh sostoyaniĭ i dissotsiatisii mnogoatomnykh molekul v sil'nom IK lazernom pole (On the Mechanism of Excitation of High Vibrational States and Dissociation of Polyatomic Molecules in a Strong Infrared Laser Field), Preprint No. 58, Lebedev Physics Institute, Academy of Sciences of the USSR, M., 1978.

[9] V. N. Bagratashvili, Yu. G. Vaĭner, V. S. Dolzhikov, S. F. Kol'yakov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, É. G. Sil'kis, and V. D. Titov, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 502 (1979) [JETP Lett. **30**, 471 (1979)].

[10] G. A. Askar'yan, Zh. Eksp. Teor. Fiz. **46**, 403 (1964); **48**, 666 (1965) [Sov. Phys. JETP **19**, 273 (1964); **21**, 439 (1965)]; F. V. Bunkin, R. V. Karapetyan, and A. M. Prokhorov, Zh. Eksp. Teor. Fiz. **47**, 216 (1964) [Sov. Phys. JETP **20**, 145 (1965)].

[11] V. I. Gorchakov and V. N. Sazonov, Zh. Eksp. Teor. Fiz. **70**, 467 (1976) [Sov. Phys. JETP **43**, 241 (1976)]; V. I. Sazonov and V. Yu. Finkel'shteĭn, Dokl. Akad. Nauk. SSSR **231**, 78 (1976)[Sov. Phys. Dokl. **21**, 645 (1976)].

[12] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and B. G. Sartakov, Zh. Eksp. Teor. Fiz. **72**, 88 (1977) [Sov. Phys. JETP **45**, 47 (1977)].

[13] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and B. G. Sartakov, Zh. Eksp. Teor. Fiz. **74**, 490 (1978) [Sov. Phys. JETP, 257 (1978)].

[14] A. V. Eletskiĭ, V. D. Klimov, and V. A. Legasov, Dokl. Akad. Nauk SSSR **237**, 1396 (1977).

[15] K. L. Kompa, P. L. F. Jahresbericht, No. 39-71, Munich, 1977; J. L. Lyman, J. Chem. Phys. **67**, 1868 (1977).

[16] V. T. Platonenko, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 52 (1977) [Sov. Phys. JETP **25**, 46 (1977)].

[17] V. S. Letokhov, in: Multiphoton Processes (Proc. First Intern. Conf. University of Rochester, N. Y., 1977, ed. by J. H. Eberly and P. Lambropoulos), Wiley, New York (1978), p. 331.

[18] S. S. Alimpiev, N. V. Karlov, B. G. Sartakov, and E. M. Khokhlov, Opt. Commun. **26**, 45 (1978).

[19] P. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, A. A. Puretskiĭ, and N. P. Furzikov, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 217 (1976) [JETP Lett. **23**, 194 (1976)].

[20] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, A. M. Prokhorov, B. G. Sartakov, and É. M. Khokhlov, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 428 (1977) [JETP Lett. **25**, 400 (1977)].

[21] V. M. Agranovich and V. I. Rupasov, Preprint No. 11/132, Institute of Spectroscopy, Academy of Sciences of the USSR, M., 1976.

[22] É. V. Shuryak, Zh. Eksp. Teor. Fiz. **71**, 2039 (1976) [Sov. Phys. JETP **44**, 1070 (1976)].

[23] K. D. Hänsel, Chem. Phys. **33**, 35 (1978).

[24] K. T. Hecht, J. Mol. Spectrosc. **5**, 355 (1960).

[25] B. G. Sartakov, Tr. Fiz. Inst. Akad. Nauk SSSR **114**, 90 (1979).

[26] A. N. Kolmogorov, Dokl. Akad. Nauk. SSSR **98**, 527 (1954); V. I. Arnol'd, Usp. Mat. Nauk **18**, No. 6 (114), 91 (1963); G. M. Zaslavskiĭ, Statisticheskaya neobratimost' v nelineĭnykh sistemakh (Statistical Irreversibility in Nonlinear Systems), Nauka, M., 1970.

[27] A. V. Gaponov-Grekhov and M. I. Rabinovich, Usp. Fiz. Nauk **128**, 579 (1979) [Sov. Phys. Usp. **22**, 590 (1979)].

[28] S. A. Rice, in: Advances in Laser Chemistry (Proc. Conf., California Institute of Technology, Pasadena, California, 1978), Springer Verlag, Berlin (1978), p. 2; J. Ford, Adv. Chem. Phys. **24**, 155 (1973).

[29] K. Sture, J. Nordholm, and S. A. Rice, J. Chem. Phys. **61**, 203, 768 (1974).

[30] A. Kaldor, R. B. Hall, D. M. Cox, J. A. Horsley, P. Rabinowitz, G. M. Kramer, and E. B. Priestley, in: Europhysics Study Conf. on Multiphoton Processes, Benodet, France, 1979, p. 101.

[31] V. V. Bertsev, T. D. Kolomiĭtseva, and N. M. Tsyganenko, Opt. Spektrosk. **37**, 463 (1974) [Opt. Spectrosc. (USSR) **37**, 263 (1974)].

[32] R. S. McDowell, J. P. Aldridge, and R. F. Holland, J. Phys. Chem. **80**, 1203 (1976).

[33] V. N. Bagratashvili, V. S. Dolzhikov, V. S. Letokhov, A. A Makarov, E. A. Ryabov, and V. V. Tyakht, Zh. Eksp. Teor. Fiz. **77**, 2238 (1979) [Sov. Phys. JETP **50**, 1075 (1979)].

[34] V. M. Akulin, Dissertation for Candidate's Degree, M., 1980.

Translated by A. Tybulewicz