SPECIFICS OF VIBRATIONAL LEVELS OF POLYATOMIC MOLECULES

B. G. Sartakov

The discovery of the effect of collisionless dissociation of polyatomic molecules [1] and the subsequent proof of isotopic selectivity of the process [2] has aroused great interest in the problem of excitation of polyatomic molecules and made it necessary to review the previously held ideas concerning the structure of the vibrational spectrum of polyatomic molecules. The models of excitation of a molecule by a laser field [3-5] proposed prior to the discovery of the effect of collisionless dissociation and based on the vibrational spectrum of a one-dimensional oscillator cannot explain why polyatomic molecules are effectively excited without participation of collisions when acted upon at a frequency close to one of the vibrational frequencies of the molecule and dissociate when the laser-radiation intensity amounts to 10^8-10^9 W/cm^2.

Strictly speaking, the model of the one-dimensional oscillator is valid only for diatomic molecules. In the case of polyatomic molecules it is necessary to take into consideration the singularities of the vibrational spectra that distinguish it from the spectrum of the one-dimensional oscillator. The main simgularity of the vibrational spectrum of polyatomic molecules is that owing to the large number of vibrational degrees of freedom the density of the vibrational states increases rapidly with increasing vibrational energy. This leads to formation of a quasicontinuum of vibrational states, starting with a certain energy value, and this explains the effectiveness of excitation of polyatomic molecules by laser pulses having an intensity of the order 10^8-10^9 W/cm^2 [6, 7]. The subdivision of the spectrum of the vibrational states into two regions — the region of low vibrational levels and the quasicontinuum — which was carried out in [6, 7] permits a qualitatively correct description of the features of excitation of polyatomic molecules by coherent radiation.

At the same time, the vibrational spectrum has one more feature that must be taken into consideration when it comes to explaining collisionless dissociation of polyatomic molecules. This feature is that the vibrations of most polyatomic molecules are close in frequency. The agreement between the frequencies of the vibrations can be due to the symmetry of the molecules or can be accidental. As shown in [8, 9], the splitting of degenerate vibrations by the anharmonicity of the states leads to formation of a band structure of the quasicontinuum and of bands of lower levels. In contrast to the one-dimensional oscillator, the detunings produced on account of the anharmonicity cannot accumulate when such vibrations are excited. Since the detunings due to the anharmonicity do not accumulate, the polyatomic molecules can be effectively excited in fields of moderate intensity. The nonaccumulation of the detunings in the system of low levels of the SF_6 molecule was considered in [10, 11].

It is seen thus that the results of an analysis of the vibrational spectrum of polyatomic molecules serve as the basis for a theoretical explanation of the effect of isotopically selective collisionless dissociation of polyatomic molecules in a coherent radiation field. The present paper is devoted to an investigation of the vibrational spectrum of polyatomic molecules. The analysis is carried out mainly with the molecules $XY_4(T_d)$ and $XY_6(O_h)$ as examples.

1. We consider the vibrational Hamiltonian of molecules of the type XY_4 and XY_6. Just as any vibrational Hamiltonian of a system of coupled nonlinear oscillators, it has a complicated structure. Before we proceed to a determination of the energy spectrum, we simplify as much as possible the form of the Hamiltonian.

The first simplification that will be made is connected with the possibility of expanding the vibrational Hamiltonian of polyatomic molecules in powers of the Born—Oppenheimer small parameter. In the Born—Oppenheimer approximation the total Hamiltonian of any molecule can be expanded in the small parameter $\sqrt{m/M}$, where m is the electron mass and M is the pro-

---

Translated from Trudy Ordena Lenina Fizicheskogo Instituta im. P. N. Lebedeva Akademii Nauk SSSR, Vol. 114, pp. 90-106, 1979.

ton mass. This expansion makes it possible to separate the electronic, vibrational, and rotational parts of the Hamiltonian. The vibrational part of the Hamiltonian of any electronic state can also be expanded in the small parameter $\sqrt{m/M}$. The zeroth order of the expansion determines the harmonic part of the vibrational Hamiltonian, the first order determines the cubic nonlinearity, the second, the nonlinearity of fourth order, etc. The energy scale of the harmonic part, i.e., the vibrational quantum, for polyatomic molecules such as SF_6, SiF_4, OsO_4 and others, is ≈ 1000 cm^{-1}, and the corrections on account of the fourth-order nonlinearity, just as of the cubic nonlinearity, are approximately smaller by a factor $\sqrt{m/M}$ and can amount to several reciprocal centimeters. Corrections due to the nonlinearities of fifth, sixth, and higher orders depend generally speaking strongly on the number of the vibration level, and for levels below the dissociation limit of the electronic state they do not exceed the corrections resulting from the fourth-order nonlinearity. Consequently, the splitting of the levels and their displacement away from the harmonic positions are determined mainly by the anharmonicities of third and fourth orders. Therefore, without adversely affecting the analyses that follow we discard nonlinearities of order higher than the fourth from the vibrational Hamiltonian.

Now, using a one-dimensional oscillator with small cubic nonlinearity as the example, we shall show that by means of a nonlinear canonical transformation it is possible to reduce the initial Hamiltonian, accurate to quadratically small terms, to a form containing only a fourth-order nonlinearity. Let the initial Hamiltonian be of the form

$$H = \frac{p^2}{2} + \frac{x^2}{2} + axp^2 + bx^3. \tag{1}$$

For simplicity we assume that the mass and the harmonic frequency of the vibrations are equal to unity. The term bx^3 corresponds to nonlinearity of the potential energy, and the term axp^2 to the nonlinearity of the kinetic energy, which usually takes place if the vibration takes place along a curvilinear trajectory. Expansion of the Hamiltonian in powers of p cannot contain odd powers of p, since the Hamiltonian must be invariant to the time-reversal operation, and consequently to the replacement $p \to -p$. Therefore Eq. (1) is the most general form of the cubic nonlinearity of a one-dimensional oscillator.

To eliminate the cubic anharmonicity, we carry out a nonlinear canonical transformation, taking the generating function in the form

$$\Phi = Px + \alpha x^2 P + \beta P^3, \tag{2}$$

where P is the new momentum; α, β are the transformation parameters. From (2) we obtain

$$\begin{aligned} X &= \frac{\partial\Phi}{\partial P} = x + \alpha x^2 + 3\beta P^2, \\ p &= \frac{\partial\Phi}{\partial x} = P + 2\alpha P x, \end{aligned} \tag{3}$$

where X is a new coordinate. Accurate to quadratically small terms we get from (3)

$$\begin{aligned} x &= X - \alpha X^2 - 3\beta P^2 + 2\alpha^2 P^3 + 6\alpha\beta\, XP^2, \\ p &= P + 2\alpha\, PX - 2\alpha^2 PX^2 - 6\alpha\beta P^3. \end{aligned} \tag{4}$$

Substituting (4) in (1), we obtain with the same accuracy the Hamiltonian in the variables X and P:

$$\begin{aligned} H = {} & \frac{P^2}{2} + \frac{X^2}{2} + (b - \alpha) X^3 + (a + 2\alpha - 3\beta) XP^2 + \left(\frac{5\alpha^2}{2} - 3\alpha b\right) X^4 + \\ & + \left(\frac{9}{2}\beta^2 - 6\alpha\beta - 3a\beta\right) P^4 + (9\alpha\beta + 3\alpha a - 9\beta b) X^2 P^2. \end{aligned} \tag{5}$$

We take the transformation parameters

$$\alpha = b, \qquad \beta = \frac{a + 2b}{3}. \tag{6}$$

Then the cubic nonlinearity vanishes from (5) and we obtain the Hamiltonian

$$H = \frac{P^2}{2} + \frac{X^2}{2} - \frac{b^2}{2} X^4 - \frac{(a + 2b)^2}{2} P^4 + 3abX^2P^2. \tag{7}$$

When quantizing the Hamiltonian it must be remembered that it was obtained under the condition $xp - px = 0$; therefore the quantized Hamiltonian (7) can differ from the quantized Hamiltonian (1) by the inessential constant quantity $\sim \hbar^2$.

We note that the performed transformation was possible because the number of the cubic-nonlinearity constants, as well as the number of the transformation parameters, is equal to two. It is impossible in the general case to reduce by a similar transformation a nonlinearity of fourth order to a nonlinearity of higher order, since the number of terms of fourth order in the Hamiltonian is three (they are x^4, x^2p^2, p^4), and the number of parameters of transformation is two (they are the coefficients preceding the terms x^3P, xP^3 in the expression for Φ).

Generally speaking, any nonlinearity of odd order can be reduced to a nonlinearity of the next order, while a nonlinearity of even order can in general form not be eliminated. It is easy to generalize the result to include the case of a multidimensional vibrational system with a weak nonlinearity. Therefore we take an initial vibrational Hamiltonian containing a harmonic part and a weak nonlinearity of fourth order, assuming that the fundamental frequencies and the nonlinearity parameters can be determined from spectroscopic data.

All the simplifications introduced so far were general in character and were valid for any polyatomic molecule. We now take into account the features of the excitation and the symmetry of the molecules.

It is known that the interaction between laser radiation and the molecules is a dipole interaction. Therefore, in the spectrum of the energy states, it is possible to populate substantially by laser radiation only those levels that are coupled by a strong dipole moment, and between which the transition frequency is close to the laser frequency. Let the initial state in the excitation process be the ground vibrational state and let the frequency of the action be close to one of the normal frequencies of the molecule. Then the states most strongly populated will be those of the excited mode and of those compound vibrations whose frequency accidentally coincides with the laser frequency. Generally speaking, the dipole moment of the compound vibrations is substantially smaller than that of the fundamental vibration. If the state of the fundamental vibration experiences a random Fermi resonance with the level of a compound vibration, the dipole moments will be of the same order of magnitude. We therefore confine ourselves to consideration of the energy spectrum of one mode.

We separate in the Hamiltonian of the molecules $XY_4(T_d)$ and $XY_6(O_h)$ that part which corresponds to the resonantly excited mode. For both XY_4 and XY_6 molecules, the vibrations that are active in the IR band are triply degenerate. We chose the vibrational coordinates x, y, and z in such a way that they are transformed under symmetry operations in exactly the same manner as the Cartesian coordinates of the reference frames that are rigidly connected with the molecules and are shown in Fig. 1. When the coordinates are so chosen, there exist for both the XY_4 and XY_6 molecules the following three combinations of fourth degree, which transform in accordance with a fully symmetrical representation and are made up of the coordinates and momenta that can enter in the nonlinear part of the Hamiltonian:

$$x^4 + y^4 + z^4, \quad x^2y^2 + y^2z^2 + z^2x^2, \qquad (8)$$
$$([\mathbf{p} \times \mathbf{r}])^2 = \mathbf{p}^2\mathbf{r}^2 - (\mathbf{r}\cdot\mathbf{p})^2,$$

where $\mathbf{r} = (x, y, z)$; $\mathbf{p} = (p_x, p_y, p_z)$ is the momentum of the vibrational mode. Thus, the vibrational Hamiltonian of the excited mode is of the form

$$H = \mathbf{p}^2/2m + m\omega^2\mathbf{r}^2/2 + A\,(x^4 + y^4 + z^4) + B\,(x^2y^2 + y^2z^2 + z^2x^2) + C\,([\mathbf{p} \times \mathbf{r}])^2, \qquad (9)$$

where m is the effective mass of the vibrations; ω, harmonic frequency; A, B, and C, constants of the intramode anharmonicity. The obtained Hamiltonian has the same form for the molecules XY_4 and XY_6, since they are spherical tops.

2. We proceed now to determine the spectrum of the vibrational states of the obtained Hamiltonian of the degenerate mode. In the harmonic approximation, i.e., at $A = B = C = 0$, the spectrum takes the simple form

$$E_v = \hbar\omega\,(v + 3/2), \qquad (10)$$

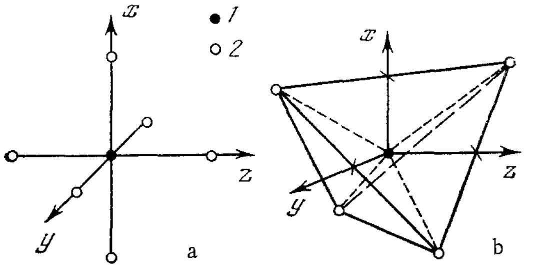

Fig. 1. General form of the molecules XY_6 (a) and XY_4 (b). 1) The atom X, b) the atom Y. The arrows show the Cartesian axes rigidly bound to the molecules.

where ω is the frequency of the vibrations in the harmonic approximation; v is the vibrational quantum number. Each energy level except the ground level is degenerate. The degeneracy multiplicity is given by

$$g_v = (v+1)(v+2)/2. \tag{11}$$

The degeneracy is the consequence of the spherical symmetry of the harmonic part of the Hamiltonian, and is lifted if perturbations that violate this symmetry are present. The lifting of spherical symmetry leads to a splitting of the degenerate level [12] into as many sublevels as there should exist in accordance with the group symmetry of the interaction that causes this splitting.

In the presently considered case, the correction to the harmonic part of the Hamiltonian, both for the XY_4 and for the XY_6 molecules, is of the same form, and accordingly the number of sublevels into which the splitting takes place is the same in both cases. We shall classify the sublevels into which the splitting takes place in accord with the types of symmetry of the group T_d. To change over to classification in accordance with types of symmetry of the group O_h, the following rule is available. If v is even, then the type of symmetry does not change and an index g is added to indicate that the sign of the wave function is not changed by the inversion operation contained in the O_h group. If v is odd, then the level symmetry types change in accordance with the rule

$$A_1 \leftrightarrow A_2, \quad E \leftrightarrow E, \quad F_1 \leftrightarrow F_2 \tag{12}$$

and an index u is added to indicate that the wave function reverses sign under the inversion operation.

The splitting of the degenerate levels is the main feature that distinguishes the three-dimensional oscillator from the one-dimensional one, and plays a principal role in the analysis that follows. Whereas in the case of a one-dimensional oscillator the anharmonicity shifts the single level from the harmonic position, and this shift accumulates with increasing vibrational quantum number v, increasing in proportion to v^2, in the case of a three-dimensional oscillator, the splitting produces a band of levels, the edges of which can move in opposite directions away from the harmonic position of the level, and in this case the detuning due to the anharmonicity is not cumulative.

To find the degenerate-state splitting due to the anharmonic part of the Hamiltonian

$$\hat{H}_{\text{anh}} = A\,(x^4 + y^4 + z^4) + B\,(x^2y^2 + y^2z^2 + z^2x^2) + C\,([\mathbf{p} \times \mathbf{r}])^2, \tag{13}$$

we use perturbation theory. To this end it is necessary to choose the zeroth-approximation wave functions. In connection with the degeneracy, this choice is ambiguous. We take as the zeroth approximation the wave functions of three one-dimensional oscillators, each of which corresponds to vibrational motion along one of the Cartesian axes of the molecule. The spectrum of the eigenvalues of the one-dimensional oscillator takes the simple form

$$E_{v_i} = \hbar\omega\,(v_i + 1/2), \tag{14}$$

where v_i is the vibrational quantum number of the i-th one-dimensional oscillator, and the wave function is expressed in terms of a Hermite polynomial

$$\psi_{v_i}(r_i) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \exp\left(-\frac{m\omega r_i^2}{2\hbar}\right) H_{v_i}\left(r_i \sqrt{\frac{m\omega}{\hbar}}\right). \tag{15}$$

The wave function of a three-dimensional oscillator in the harmonic approximation is the product of the wave functions of three one-dimensional oscillators

$$|v_x, v_y, v_z\rangle = \psi_{v_x}(x)\,\psi_{v_y}(y)\,\psi_{v_z}(z), \tag{16}$$

and the connection between the vibrational quantum numbers is of the simple form

$$v = v_x + v_y + v_z.$$

When finding the corrections of the first approximation of perturbation theory for the degenerate states, it is necessary to solve the secular equation [13]. We seek the eigenfunctions in the form

$$\psi = \sum_{v_x+v_y+v_z=v} b_{v_xv_yv_z} \,|\, v_x, v_y, v_z\rangle', \tag{17}$$

where $|\, v_x, v_y, v_z\rangle' = (v_x!\, v_y!\, v_z!)^{-1/2}\, |v_x, v_y, v_z\rangle$. The coefficients $b_{v_xv_yv_z}$ are elements of a vector-column of the ψ function in the new basis. For the coefficients $b_{v_xv_yv_z}$ and for the correction ε to the harmonic value of the energy we obtain the equation

$$\varepsilon\psi = \hat{H}_{\text{anh}}\psi. \tag{18}$$

$$\langle v_x, v_y, v_z \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \alpha \sum_i v_i^2 + \beta\,(v_xv_y + v_yv_z + v_zv_x),$$

$$\langle v_x - 2, v_y + 2, v_z \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \langle v_x, v_y + 2, v_z - 2 \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \gamma\,(v_y + 1)(v_y + 2),$$

The matrix elements $\hat{H}_{\text{anh}}$ in the basis $|v_xv_yv_z\rangle'$ take the form

$$\begin{gathered}\langle v_x + 2, v_y - 2, v_z \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \langle v_x + 2, v_y, v_z - 2 \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \gamma\,(v_x + 1)(v_x + 2),\\ \langle v_x - 2, v_y, v_z + 2 \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \langle v_x, v_y - 2, v_z + 2 \,|\, \hat{H}_{\text{anh}} \,|\, v_x, v_y, v_z\rangle' = \gamma\,(v_z + 1)(v_z + 2),\end{gathered} \tag{19}$$

where

$$\alpha = 6A\,(\hbar/2m\omega)^2, \qquad \beta = 4B\,(\hbar/2m\omega)^2 + 2C\hbar^2, \qquad \gamma = B\,(\hbar/2m\omega)^2 - C\hbar^2. \tag{20}$$

In (19) we retained only the terms quadratic in v, since the linear and constant terms lead to an inessential redefinition of the frequency and to a small shift of the energy origin.

Equation (18) is solved with the aid of the generating functions

$$\Phi = \sum_{v_x+v_y+v_z=v} x^{v_x} y^{v_y} z^{v_z} b_{v_xv_yv_z}. \tag{21}$$

Here x, y, and z are generally speaking formal parameters. From (18) we obtain for Φ the equation

$$\varepsilon\Phi = \hat{\mathcal{L}}\Phi \equiv \Big[(\alpha - \beta/2 - \gamma) \sum_{s=x,\,y,\,z} \Big(s\frac{\partial}{\partial s}\Big)^2 + (\beta/2)\Big(\sum_{s=x,\,y,\,z} s\frac{\partial}{\partial s}\Big)^2 + \gamma\Big(\sum_{s=x,\,y,\,z} s\Big)^2\Big(\sum_{s=x,\,y,\,z}\frac{\partial^2}{\partial s^2}\Big)\Big]\Phi, \tag{22}$$

the solution of which is a polynomial of degree v.

Before we proceed to solve (22), we break up the space of the polynomials of degree v into subspaces, each of which is transformed in accordance with an irreducible representation of the group T_d. We note that any polynomial of degree v is transformed under symmetry operations as if x, y, and z were real Cartesian coordinates of a reference frame rigidly tied to the molecule. We choose the initial basis in polynomial space in the form

$$\mathbf{e}_i = x^{v_x} y^{v_y} z^{v_z}. \tag{23}$$

Let k = min (v_x, v_y, v_z). All the basis vectors with identical k will be referred to a single subspace $P_v{}^k$. In this subspace, any basis vector can be represented in the form

$$\mathbf{e}_i = \begin{cases} (xyz)^k\, x^m y^n, \\ (xyz)^k\, y^m z^n, \\ (xyz)^k\, z^m x^n. \end{cases} \tag{24}$$

In the chosen Cartesian reference frames, both for the XY_4 and for the XY_6 molecules, each operation of the symmetry of the group T_d reduces either to a permutation of the Cartesian coordinates or to a reversal of the signs of two of them, or else to a simultaneous performance of these operations. Therefore the product (xyz) is not changed by the symmetry operations, and a product of the form $(x^m y^n)$ goes over either into itself or into one of the products

$$(x^m z^n), \quad (z^m y^n), \quad (y^m x^n), \quad (z^m x^n), \quad (y^m z^n).$$

Let $m > n \neq 0$, and then we have six basis vectors, which for given k, m, and n are transformed into one another under symmetry operations, and a corresponding six-dimensional subspace invariant with respect to symmetry operations. From the six basis vectors

$$\begin{aligned} &[(xyz)^k x^m y^n], \quad [(xyz)^k y^m x^n], \\ &[(xyz)^k y^m z^n], \quad [(xyz)^k z^m y^n], \\ &[(xyz)^k z^m x^n], \quad [(xyz)^k x^m z^n] \end{aligned}$$

it is easy to construct a basis of irreducible subspaces. If m and n are even, then the vector

$$A_1^{kmn} = (xyz)^k (x^m y^n + y^m x^n + z^m y^n + y^m z^n + x^m z^n + z^m x^n) \tag{25}$$

is the basis vector of a one-dimensional subspace that transforms in accordance with the representation A_1 while the vector

$$A_2^{kmn} = (xyz)^k [x^m y^n + y^m z^n + z^m x^n - x^n y^m - y^n z^m - x^m z^n] \tag{26}$$

is a basis of the subspace that transforms in accordance with the representation A_2. The vectors

$$\begin{aligned} E_{a1}^{kmn} &= (xyz)^k [2y^m z^n + 2z^m y^n - x^m z^n - z^m x^n - x^m y^n - y^m x^n], \\ E_{b1}^{kmn} &= (xyz)^k [x^m z^n + z^m x^n - x^m y^n - y^m x^n] \end{aligned} \tag{27}$$

form the basis of a two-dimensional subspace that transforms in accordance with the representation E. Analogously, the basis of the E-subspace is made up by the vectors

$$\begin{aligned} E_{a2}^{kmn} &= (xyz)^k [z^m x^n - x^m z^n - x^m y^n + y^m x^n], \\ E_{b2}^{kmn} &= (xyz)^k [2y^m z^n - 2z^m y^n - z^m x^n + x^m z^n - y^n x^m + y^m x^n]. \end{aligned} \tag{28}$$

The matrices of the symmetry operators in both E-subspaces are the same and do not depend on the set of numbers k, m, and n.

If m and n are both odd, then the vectors

$$\begin{aligned} F_{1x}^{kmn} &= (xyz)^k (y^m z^n - z^m y^n), \\ F_{1y}^{kmn} &= (xyz)^k (z^m x^n - x^m z^n), \\ F_{1z}^{kmn} &= (xyz)^k (x^m y^n - y^m x^n) \end{aligned} \tag{29}$$

form the basis of a three-dimensional irreducible subspace that transforms in accordance with the representation F_1, while the vectors

$$\begin{aligned} F_{2x}^{kmn} &= (xyz)^k (y^m z^n + y^n z^m), \\ F_{2y}^{kmn} &= (xyz)^k (x^m z^n + z^m x^n), \\ F_{2z}^{kmn} &= (xyz)^k (x^m y^n + x^n y^m) \end{aligned} \tag{30}$$

form the basis of a subspace that transforms in accordance with the representation F_2. If m is even and n is odd (the case of odd m and even n is accounted for by interchanging m and n in the formulas), then the vectors

$$\begin{aligned} F_{1x}^{kmn} &= (xyz)^k (y^m - z^m) x^n, \\ F_{1y}^{kmn} &= (xyz)^k (z^m - x^m) y^n, \\ F_{1z}^{kmn} &= (xyz)^k (x^m - y^m) z^n \end{aligned} \tag{31}$$

are the basis of the F_1 subspace, and the vectors

$$\begin{aligned} F_{2x}^{kmn} &= (xyz)^k (y^m + z^m) x^n, \\ F_{2y}^{kmn} &= (xyz)^k (z^m + x^m) y^n, \\ F_{2z}^{kmn} &= (xyz)^k (x^m + y^m) z^n \end{aligned} \tag{32}$$

are the basis of the F_2 subspace. The matrices of the symmetry operators in the like subspaces do not depend on the set of numbers k, m, and n.

If $m = n \neq 0$, then in the case of odd numbers m and n the F_1 subspace vanishes, and in the case of even m and n one E subspace and the A_2 subspace vanish. If $m = n = 0$, then $v = 3k$ is divided by three and the subspace $P_v^{v/3}$ is irreducible and transforms in accordance with the representation A_1.

Thus, we have covered all the cases of different relations between the numbers k, m, and n, and the subspace of polynomials of degree v is broken up into irreducible subspaces.

This breakup greatly simplifies the determination of the solution of Eq. (22). In fact, the operator $\hat{\mathscr{L}}$ is invariant to the operations of the symmetry of the group T_d. It therefore cannot change the symmetries of the chosen bases vectors. Moreover, in the case of multidimensional representations it can transform into one another only the basis vectors with identical indices ($a \to a$, $x \to x$ etc.). Consequently to find the energy eigenvalues $\varepsilon(\Gamma_i)$ of the levels of a certain type of symmetry Γ_i it suffices to determine the type of matrix $\hat{\mathscr{L}}$ in the basis of the generating functions of this type of symmetry and find its eigenvalues.

For the molecules $XY_4(T_d)$ and $XY_6(O_h)$ the number of sublevels of one type of symmetry becomes larger than two, starting with $v = 5$. Therefore up to $v = 4$, when the generating functions are broken up by symmetry type, there is no need for solving algebraic equations of degree higher than two in order to find the corrections ε.

For $v = 0, 1, 2$ it is not necessary to solve even quadratic equations. In fact, in the case $v = 0$ there is one symmetry level A_1. It corresponds to the generating function $\Phi = 1$. Substituting it in (22), we get $\varepsilon = 0$. The level $v = 1$ has the symmetry F_2, the generating function $F_{2x}^{0,1,0} = x$ and $\varepsilon(v = 1, F_2) = \alpha$.

The band $v = 2$ includes the sublevels $A_1 + E + F_2$. Taking the generating functions

$$A_1^{0,2,0} = x^2 + y^2 + z^2, \qquad E_b^{0,2,0} = y^2 - z^2, \qquad F_{2x}^{0,1,1} = yz,$$

we obtain from (22)

$$\varepsilon(v = 2, A_1) = 4\alpha + 4\gamma, \qquad \varepsilon(v = 2, E) = 4\alpha - 2\gamma, \qquad \varepsilon(v = 2, F_2) = 2\alpha + \beta.$$

We consider now the band $v = 3$. It consists of four sublevels $A_1 + F_1 + 2 \times F_2$. Choosing the basis generating functions in the form

$$A_1^{1,0,0} = xyz, \qquad F_{1x}^{0,2,1} = y^2x - z^2x, \qquad F_{2x}^{0,3,0} = x^3, \qquad F_{2x}^{0,2,1} = (y^2 + z^2)\,x,$$

we find that

$$\varepsilon(v = 3, A_1) = 3\alpha + 3\beta, \qquad \varepsilon(v = 3, F_1) = 5\alpha + 2\beta - 2\gamma.$$

The matrix of the operator $\hat{\mathscr{L}}$ in the basis of the functions of symmetry F_2 is of the form

$$\hat{\mathscr{L}} = \begin{pmatrix} 9\alpha & 6\gamma \\ 4\gamma & 5\alpha + 2\beta + 2\gamma \end{pmatrix}.$$

Its eigenvalues determine the position of the levels of symmetry F_2:

$$\varepsilon\,(v = 3, F_2) = 7\alpha + \beta + \gamma \pm [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}.$$

The band $v = 4$ is split into seven sublevels $2 \times A_1 + 2 \times E + F_1 + 2 \times F_2$. The operator $\hat{\mathscr{L}}$ in the basis of functions of symmetry A_1

$$A_1^{0,4,0} = x^4 + y^4 + z^4, \qquad A_1^{0,2,2} = x^2y^2 + y^2z^2 + z^2x^2$$

is of the form

$$\hat{\mathscr{L}} = \begin{pmatrix} 16\alpha & 24\gamma \\ 4\gamma & 8\alpha + 4\beta + 4\gamma \end{pmatrix}.$$

Diagonalizing the matrix $\hat{\mathscr{L}}$, we obtain

$$\varepsilon\,(v = 4, A_1) = 12\alpha + 2\beta + 2\gamma \pm 2\,[(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}.$$

Choosing basis functions of symmetry E in the form

$$E_b^{0,4,0} = z^4 - y^4, \qquad E_b^{0,2,2} = (z^2 - y^2)\,x^2,$$

TABLE 1

v	ε	Φ
0	0	1
1	α	$x; \quad y; \quad z$
2	$4\alpha + 4\gamma$	$x^2 + y^2 + z^2$
	$4\alpha - 2\gamma$	$2x^2 - y^2 - z^2; \quad y^2 - z^2$
	$2\alpha + \beta$	$yz; \quad xz; \quad xy$
3	$3\alpha + 3\beta$	xyz
	$5\alpha + 2\beta - 2\gamma$	$(y^2 - z^2)\,x; \quad (z^2 - x^2)\,y; \quad (x^2 - y^2)\,z$
	$7\alpha + \beta + \gamma \pm [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}$	$-6\gamma x^3 + \{2\alpha - \beta - \gamma \mp [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}\}\,(y^2 + z^2)\,x$ $-6\gamma y^3 + \{2\alpha - \beta - \gamma \mp [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}\}\,(z^2 + x^2)\,y$ $-6\gamma z^3 + \{2\alpha - \beta - \gamma \mp [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}\}\,(\;^2 + y^2)\,z$
4	$12\alpha + 2\beta + 2\gamma \pm 2\,[(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}$	$12\gamma\,(x^4 + y^4 + z^4) + \{\beta + \gamma - 2\alpha \pm [(\beta + \gamma - 2\alpha)^2 + 24\gamma^2]^{1/2}\}\,(x^2y^2 + y^2z^2 + z^2x^2)$
	$12\alpha + 2\beta - \gamma \pm [(2\beta - 4\alpha - \gamma)^2 + 24\gamma^2]^{1/2}$	$12\gamma\,(y^4 - z^4) + \{2\beta - 4\alpha - \gamma \pm [(2\beta - 4\alpha - \gamma)^2 + 24\gamma^2]^{1/2}\}\,(y^2 - z^2)\,x^2$ $12\gamma\,(2x^4 - y^4 - z^4) - \{2\beta - 4\alpha - \gamma \pm [(2\beta - 4\alpha - \gamma)^2 + 24\gamma^2]^{1/2}\}\,(2y^2z^2 - y^2x^2 - z^2x^2)$
	$10\alpha + 3\beta - 6\gamma$	$yz\,(y^2 - z^2); \quad xz\,(z^2 - x^2); \quad xy\,(x^2 - y^2)$
	$8\alpha + 4\beta + 3\gamma \pm [(2\alpha - \beta + 3\gamma)^2 + 24\gamma^2]^{1/2}$	$2\gamma x^2yz + \{2\alpha - \beta + 3\gamma \pm [(2\alpha - \beta + 3\gamma)^2 + 24\gamma^2]^{1/2}\}\,yz\,(y^2 + z^2)$ $2\gamma xy^2z + \{2\alpha - \beta + 3\gamma \pm [(2\alpha - \beta + 3\gamma)^2 + 24\gamma^2]^{1/2}\}\,xz\,(x^2 + z^2)$ $2\gamma xyz^2 + \{2\alpha - \beta + 3\gamma \pm [(2\alpha - \beta + 3\gamma)^2 + 24\gamma^2]^{1/2}\}\,xy\,(x^2 + y^2)$

we obtain similarly

$$\varepsilon\,(v=4,\ E)=12\alpha+2\beta-\gamma\pm[(2\beta-4\alpha-\gamma)^2+24\gamma^2]^{1/2}.$$

For the F_1 sublevel we choose the generating function $F^{0,\ 3,\ 1}_{1z} = x^3y - y^3x$. Substituting it in (22), we obtain $\varepsilon(v = 4,\ F_1) = 10\alpha + 3\beta - 6\gamma$. In the basis of the generating functions of symmetry F_2

$$F^{1,1,0}_{2x}=x^2yz,\qquad F^{0,3,1}_{2x}=y^3z+z^3y$$

the operator $\hat{\mathscr{L}}$ takes the form

$$\hat{\mathscr{L}}=\begin{pmatrix}6\alpha+5\beta & 2\gamma\\ 12\gamma & 10\alpha+3\beta+6\gamma\end{pmatrix}.$$

Its eigenvalues are equal to

$$\varepsilon\,(v=4,\ F_2)=8\alpha+4\beta+3\gamma\pm[(2\alpha-\beta+3\gamma)^2+24\,\gamma^2]^{1/2}.$$

In Table 1 are gathered the energy eigenvalues ε obtained in this manner and the corresponding generating functions.

We now consider the scheme of symmetry-allowed dipole transitions between levels from 0 to $v = 4$ inclusive, which is shown in Fig. 2. In the general case the dipole moments of the transitions indicated by the arrows are not equal to zero. It is seen from the scheme that on account of successive single-quantum transitions it is possible to populate any vibrational sublevel. It becomes possible in this connection to determine the three constants of the intramode anharmonicity by methods of two-frequency IR spectroscopy [14]. Indeed, to determine α, β, γ it suffices to establish the position and the symmetry types of the three sublevels of the band $v = 2$. Two-frequency resonances yield direct information on the position of the sublevels. The symmetry types of the sublevels can be determined from the ratio of the dipole moments of the transitions from the level $v = 1$ to the sublevels of the band $v = 2$.

Let us see what the theoretical relations between the dipole moments of the transitions should be. Let the initial state be the level of the band $v = 1$ whose ψ function is equal to $|1, 0, 0\rangle$. In the harmonic approximation the nonzero matrix elements of the dipole-moment operator are of the form

$$\begin{aligned}\langle v_x+1, v_y, v_z\,|\,d_x\,|\,v_x, v_y, v_z\rangle &= d_{01}\sqrt{v_x+1},\\ \langle v_x, v_y+1, v_z\,|\,d_y\,|\,v_x, v_y, v_z\rangle &= d_{01}\sqrt{v_y+1},\\ \langle v_x, v_y, v_z+1\,|\,d_z\,|\,v_x, v_y, v_z\rangle &= d_{01}\sqrt{v_z+1},\end{aligned}\tag{33}$$

where d_{01} is the dipole moment of the 0–1 transition. Now, using the previously obtained generating functions of each of the sublevels A_1, E, F_2, we determine the corresponding wave functions. The sublevel A_1 is not degenerate and corresponds to the vibrational eigenfunction

$$|A_1\rangle=\frac{1}{\sqrt{3}}(|2,0,0\rangle+|0,2,0\rangle+|0,0,2\rangle).$$

The sublevel E is doubly degenerate and includes two states:

$$|E_a\rangle=\frac{1}{\sqrt{6}}(2|2,0,0\rangle-|0,2,0\rangle-|0,0,2\rangle),$$

$$|E_b\rangle=\frac{1}{\sqrt{2}}(|0,2,0\rangle-|0,0,2\rangle).$$

The triply degenerate level F_2 includes three states:

$$|F_{2x}\rangle=|0,1,1\rangle,\qquad |F_{2y}\rangle=|1,0,1\rangle,$$
$$|F_{2z}\rangle=|1,1,0\rangle.$$

The matrix elements of the dipole-moment operator for transitions from the level $|1, 0, 0\rangle$ to the sublevels A_1, E, F_2, which differ from zero, are equal to

$$\begin{aligned}&\langle A_1|d_x|1,0,0\rangle=\sqrt{\frac{2}{3}}\,d_{01},\qquad \langle E_a|d_x|1,0,0\rangle=\frac{2}{\sqrt{3}}\,d_{01},\\ &\langle E_{2y}|d_z|1,0,0\rangle=d_{01},\qquad \langle F_{2z}|d_y|1,0,0\rangle=d_{01}.\end{aligned}\tag{34}$$

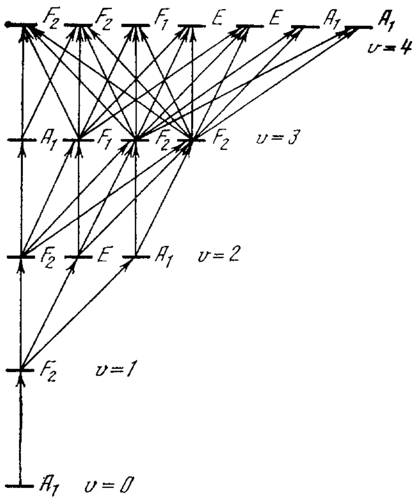

Fig. 2. Scheme of symmetry-allowed transitions between the bands of the molecules XY_4 and XY_6 from v = 0 to v = 4. The allowed transitions are shown by arrows.

Comparing the experimental ratios of the strengths of the dipole moments of the transitions with the theoretical ones, we can determine the symmetry type of each sublevel. This additional information is perfectly sufficient to determine the intramode anharmonicity constants. Generally speaking, with the aid of the generating functions we can determine the dipole moments of the transitions between the bands from v = 0 to v = 4 and more and also the positions of the sublevels in any band, but these calculations call for the use of a computer and consequently for knowledge of the concrete values of the intramode anharmonicity constants.

3. Owing to the anharmonicity splitting of the degenerate levels, the detunings from resonance with the laser radiation may not accumulate with increasing v. It is quite easy to choose a radiation frequency such that the detunings do not accumulate in the system of the lower levels. In order for the detunings not to accumulate in the system of the upper bands (v > 4) it is necessary to satisfy definite conditions for the intramode anharmonicity constants.

Let us find under which conditions no detunings due to anharmonicity in the system of the upper levels take place for molecules XY_4 and XY_6. We start from the fact that the off-diagonal elements in the matrix $\hat{H}_{anh}$ are much smaller than the diagonal ones, i.e., $\gamma \ll \alpha$ or β. Then, neglecting the off-diagonal terms, we find that the position of the band levels is uniquely determined by the set of three quantum numbers v_x, v_y, v_z with the condition $v = v_x + v_y + v_z$. The correction ε to the harmonic values of the energy $E_v = \hbar\omega\,(v + {}^3/_2)$ for the band levels depends on the set of quantum numbers in the following manner:

$$\varepsilon(v_x, v_y, v_z) = \alpha(v_x^2 + v_y^2 + v_z^2) + \beta(v_xv_y + v_yv_z + v_zv_x). \tag{35}$$

Let $v \gg 1$; then v_x, v_y, v_z can be regarded as continuous variables, which vary in the ranges $0 \leqslant v_x \leqslant v$, $0 \leqslant v_y \leqslant v$, $0 \leqslant v_z \leqslant v$ and are connected by the relation $v = v_x + v_y + v_z$.

The correction ε as a function of the variables v_x, v_y, v_z has in the range of their variation three extrema:

$$\begin{aligned} &\varepsilon_1 = \alpha v^2 \quad (v_i = v;\ i = x, y, z),\\ &\varepsilon_2 = (\alpha + \beta)\,v^2/3 \quad (v_x = v_y = v_z = v/3),\\ &\varepsilon_c = (2\alpha + \beta)\,v^2/4 \quad (v_i = v_j = v/2,\ i \neq j). \end{aligned} \tag{36}$$

The extremal values ε_1 and ε_2 determine the positions of the edges of the bands, and ε_c determines the position of the center of gravity. Indeed, at arbitrary α and β the value of ε_c lies between ε_1 and ε_2. In addition, ε_c is, accurate to terms quadratic in v, the trace of the matrix $\hat{H}_{anh}$, divided by the number of levels in the band. It is known that the trace of a matrix is the sum of its eigenvalues; therefore ε_c is the center of gravity of the band. In order for the detunings that are produced on account of the anharmonicity not to accumulate, it is necessary that ε_1 and ε_2 be of opposite sign, and then the harmonic value of the energy lies in the band. From (36) we find that to this end the constants of the intramode anharmonicity must satisfy the conditions

$$\operatorname{sign}(\alpha, \beta) = -1, \ |\alpha| < |\beta|. \tag{37}$$

Conditions (37) are the criterion for nonaccumulation of the detunings.

4. We consider now the level-density distribution in the bands, which is an important characteristic of the band structure of the quasicontinuum. The effectiveness of excitation of the molecules depends substantially on the level density near the energy $n\hbar\omega_L$, where $n = 0, 1, 2, \ldots$; ω_L is the frequency of the laser pulse. Indeed, the only band levels that can be substantially populated are those whose energy is close to $n\hbar\omega_L$. The distance from the energy value $n\hbar\omega_L$ to the nearest level of the band has generally speaking a random dependence on v, but it cannot exceed half the distance between neighboring levels in the vicinity of the energy $n\hbar\omega_L$. The higher the level density at the point $n\hbar\omega_L$, the smaller the detuning from resonance with the radiation of the nearest level of the band, and the easier it is to populate the levels close to resonance with the radiation. From the foregoing reasoning it is seen that for an effective excitation of molecules the frequency ω_L must be chosen such that the values of the energy $n\hbar\omega_L$ be located in the region of bands with maximum level density, when the rate of acquisition of energy by the molecules is maximal.

We obtain now the level-density distribution in the bands of molecules XY_4 and XY_6, in the previously assumed approximation $\gamma \ll \alpha$ or β. In this approximation, the spectrum is described by expression (35). Assuming that the vibrational quantum numbers v_i are continuous variables, we obtain first the number of levels in the band v:

$$N_v = \sum_{v_x=0}^{v} \sum_{v_y=0}^{v} \sum_{v_z=0}^{v} \delta(v - v_x - v_y - v_z) = \int_0^v dv_1 \int_0^v dv_2 \int_0^v dv_3 \delta(v - v_1 - v_2 - v_3) = \frac{v^2}{2}. \tag{38}$$

This formula corresponds to formula (11) previously obtained in the harmonic approximation, and the δ symbol under the summation sign is equal to unity at $v = v_x + v_y + v_z$ and to zero in all other cases. On going over to continuous variables, this symbol turns into the Dirac δ function. We now determine the number of states in the band v which are located in the vicinity of the energy value ε. To this end it is necessary to introduce under the summation sign in (38) one more δ symbol, viz. $\delta\left(\varepsilon - \alpha \sum_{s=x,y,z} v_s^2 - \beta(v_x v_y + v_y v_z + v_z v_x)\right)$. On going to continuous variables, it also turns into the Dirac δ function and the sum goes over into an integral that determines the level density in the band in the vicinity of the energy ε:

$$g_v(\varepsilon) = \int_0^v dv_1 \int_0^v dv_2 \int_0^v dv_3 \delta(v - v_1 - v_2 - v_3)\, \delta\left(\varepsilon - \alpha \sum_{i=1}^{3} v_i^2 - \beta(v_1 v_2 + v_2 v_3 + v_3 v_1)\right). \tag{39}$$

Since the three-dimensional integral contains two δ functions, it reduces to one-dimensional. It is seen from (39) that integration in the cube $0 \leqslant v_1 \leqslant v$, $0 \leqslant v_2 \leqslant v$, $0 \leqslant v_3 \leqslant v$ reduces to integration over a triangle with vertices (v, 0, 0), (0, v, 0), (0, 0, v). It is therefore more convenient to change over to the cylindrical coordinates z, ρ, φ with the aid of the transformation

$$v_i = \frac{z}{\sqrt{3}} + \sqrt{\frac{2}{3}}\rho \cos\left(\varphi + \frac{2\pi i}{3}\right). \tag{40}$$

The integral (39) reduces to an integral over a triangle in the polar coordinates ρ and φ :

$$g_v(\varepsilon) = \int_\Delta \rho\, d\rho\, d\varphi \frac{1}{\sqrt{3}} \delta\left(\varepsilon - \frac{\alpha + \beta}{3} v^2 - \frac{2\alpha - \beta}{2} \rho^2\right) = \frac{1}{\sqrt{3}\,|2\alpha - \beta|} \int d\varphi. \tag{41}$$

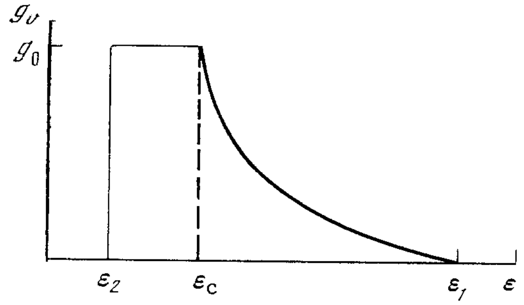

Fig. 3. Distribution of the level density in the band v. The ordinates are the level densities $g_v(\varepsilon)$ in normal units. The abscissas are the detuning from the harmonic value of the energy in arbitrary units.

The last integral is taken over arcs of a circle of radius $\rho_0 = \sqrt{2\frac{3\varepsilon-(\alpha+\beta)v^2}{3(2\alpha-\beta)}}$, which are located inside the triangle (the centers of the circle and of the triangle coincide). As a result we find that in the energy region between $\varepsilon_2 = (\alpha + \beta)v^2/3$ and $\varepsilon_c = (2\alpha + \beta)v^2/4$ the level density is constant and is given by

$$g_v(\varepsilon) = g_0 \equiv \frac{2\pi}{\sqrt{3}\,|2\alpha-\beta|}\,. \tag{42}$$

In the region between $\varepsilon_c = (2\alpha + \beta)v^2/4$ and $\varepsilon_1 = \alpha v^2$ the level density decreases monotonically from the value g_0 at $\varepsilon = \varepsilon_c$ to zero at $\varepsilon = \varepsilon_1$, in accordance with the law

$$g_v(\varepsilon) = g_0\left[1 - \frac{3}{\pi}\arccos\sqrt{\left|\frac{(2\alpha-\beta)v^2}{12\varepsilon-(4\alpha+4\beta)v^2}\right|}\right]. \tag{43}$$

We note that the energy values ε_1, ε_2, and ε_c correspond, respectively, to the edges and to the gravity centers of the bands. At the center of gravity of a band a change takes place in the character of the $g_v(\varepsilon)$ dependence. The distributions of the level density in the bands with different v are similar to one another. The form of the distribution is shown in Fig. 3.

5. We examine now the distribution of the strengths of the dipole moments among the transitions between neighboring bands of degenerate vibrations of molecules XY_4 and XY_6. To this end we sum the squares of the dipole moments of the transition from states in the vicinity of the energy ε of the band v into states lying in the vicinity of the energy ε' of the band (v + 1). If the sum differs from zero, this means that there are allowed transitions, and if it is equal to zero then there are no allowed transitions. In addition, the sum of the squares of the dipole moments determines the cross section for photon absorption in the continuous spectrum. The sum of the squares of the dipole moments, as well as of the level density in the bands, will be estimated in the approximation $v \gg 1$, $\gamma \ll \alpha, \beta$:

$$\begin{aligned} S = {} & \sum_{v_1=0}^{v}\sum_{v_2=0}^{v}\sum_{v_3=0}^{v}\sum_{v_1'=0}^{v+1}\sum_{v_2'=0}^{v+1}\sum_{v_3'=0}^{v+1}\delta\left[\sum_{i=1}^{3}v_i - v\right]\delta\left[\sum_{i=1}^{3}v_i' - v - 1\right]\times \\ & \times\delta\left[\varepsilon - \alpha\sum_{i=1}^{3}v_i^2 - \beta(v_1v_2+v_2v_3+v_3v_1)\right]\delta\left[\varepsilon' - \alpha\sum_{i=1}^{3}v_i'^2 - \beta(v_1'v_2'+v_2'v_3'+\right. \\ & \left.+v_3'v_1')\right]\{d_{01}^2[(v_1+1)\delta(v_1-v_1'+1)\delta(v_2-v_2')+(v_2+1)\delta(v_1-v_1')\times \\ & \times\delta(v_2-v_2'+1)+(v_3+1)\delta(v_3-v_3'+1)\delta(v_1-v_1')]\} = \\ & = 3d_{01}^2\sum_{v_1=0}^{v}\sum_{v_2=0}^{v}\sum_{v_3=0}^{v}(v_1+1)\delta\left[\sum_{i=1}^{3}v_i - v\right]\delta\left[\varepsilon - \alpha\sum_{i=1}^{3}v_i^2 - \beta\sum_{i<j}v_iv_j\right]\times \\ & \times\delta[(\varepsilon'-\varepsilon-\beta v)-(2\alpha-\beta)v_1]. \end{aligned} \tag{44}$$

We change now from summation to integration in cylindrical coordinates, which are determined by the expressions

$$v_i = \frac{z}{\sqrt{3}} + \sqrt{\frac{2}{3}}\rho\cos\left(\varphi + \frac{2\pi}{3}i - \frac{2\pi}{3}\right). \tag{45}$$

Then the sum (44) goes over into the integral

$$S = \frac{\sqrt{3}\,d_{01}^2(\varepsilon' - \varepsilon - \beta v + 2\alpha - \beta)}{(2\alpha-\beta)\,|2\alpha-\beta|}\int d\varphi\cdot\delta\left[\varepsilon' - \varepsilon - \frac{2(\alpha+\beta)}{3}v - \sqrt{\frac{2}{3}}(2\alpha-\beta)\rho_0\cos\varphi\right], \tag{46}$$

where $\rho_0 = \sqrt{2\frac{3\varepsilon - (\alpha+\beta)v^2}{3(2\alpha-\beta)}}$, and the integral (46) is taken over arcs of a circle of radius ρ_0, which are located inside a triangle with vertices (v, 0, 0), (0, v, 0), (0, 0, v) in the space of the numbers v_1, v_2, v_3. The planes of the triangle and of the circle, as well as their centers, coincide.

As a result of the integration we obtain the following: if the initial state has an energy ε such that $\varepsilon_2 < \varepsilon < \varepsilon_c$ (it is assumed here arbitrarily that $\varepsilon_2 < \varepsilon_c < \varepsilon_1$), then the transitions are allowed in the region $\varepsilon_a < \varepsilon' < \varepsilon_b$, where

$$\begin{aligned}\varepsilon_a &= \varepsilon + \frac{2(\alpha+\beta)}{3}v - \frac{2}{3}(2\alpha-\beta)\sqrt{\frac{3\varepsilon-(\alpha+\beta)v^2}{2\alpha-\beta}},\\ \varepsilon_b &= \varepsilon + 2(\alpha+\beta)v/3 + \frac{2}{3}(2\alpha-\beta)\sqrt{\frac{3\varepsilon-(\alpha+\beta)v^2}{2\alpha-\beta}}.\end{aligned} \tag{47}$$

If $\varepsilon_c < \varepsilon < \varepsilon_1$, then transitions are allowed in the two regions — $\varepsilon_{a1} < \varepsilon' < \varepsilon_{b1}$ and $\varepsilon_{a2} < \varepsilon' < \varepsilon_{b2}$, where

$$\begin{aligned}\varepsilon_{b1} &= \varepsilon + \frac{2(\alpha+\beta)}{3}v + (2\alpha-\beta)\sqrt{\frac{2}{3}}\rho_0,\\ \varepsilon_{a1} &= \varepsilon + \frac{6\alpha+5\beta}{6}v + (2\alpha-\beta)\sqrt{\frac{6\rho_0^2-v^2}{12}},\\ \varepsilon_{b2} &= \varepsilon + \frac{6\alpha+5\beta}{6}v - (2\alpha-\beta)\sqrt{\frac{6\rho_0^2-v^2}{12}},\\ \varepsilon_{a2} &= \varepsilon + \beta v.\end{aligned} \tag{48}$$

The sum of the squares of the dipole moments is determined by the expression

$$S = \frac{2\sqrt{3}\,d_{01}^2|\varepsilon' - \varepsilon - \beta v + 2\alpha - \beta|}{(2\alpha-\beta)^2}\left\{{}^4/_9(2\alpha-\beta)[3\varepsilon-(\alpha+\beta)v^2] - \left[\varepsilon - \varepsilon' - \frac{2}{3}(\alpha+\beta)v\right]^2\right\}^{1/2}. \tag{49}$$

6. We consider now the rate of energy acquisition in the band structure of the quasicontinuum. If it is assumed that the spectrum is practically continuous, then the rate of acquisition of energy is determined by the cross section for the absorption in the bands. Let n be the number of absorbed photons; then

$$\frac{dn}{dt} = I\sigma(n), \tag{50}$$

where σ(n) is the absorption cross section of a molecule that has stored n vibrational photons; I is the intensity of the laser radiation. The absorption cross section (accurate to inessential factors that determine the dimensionality) is equal to the product of the sum of the squares of the dipole moments by the density of states at the corresponding points of the energy spectrum. In bands of triply degenerate vibrations, the level density is practically independent of the number of the band v, and consequently of the number of absorbed photons n. This is a consequence of the fact that the width of the bands and the number of levels in the bands increase in proportion to v^2, and is confirmed by the results obtained in Sec. 4.

The sum of the squares of the dipole moments of transitions from one point of the band to another point of the neighboring band depends on v and determines the dependence of σ on n. For the band v the absorption cross section σ(v) is directly proportional to [S(v→v + 1) − S(v→v − 1)], where S(v→v + 1) corresponds to transitions from the band v into the band v + 1, and S(v→v − 1) corresponds to transitions from the band v into the band (v − 1) and is taken with a minus sign. For down transitions the square of the dipole moment is proportional not to (v + 1), as for up transitions, but to v. As a result, the sum of the squares of the dipole moments for down transitions is determined by the expression

$$S(v \to v-1) = S(v \to v+1)\left|\frac{\varepsilon' - \varepsilon - \beta v}{\varepsilon' - \varepsilon - \beta v + 2\alpha - \beta}\right|, \tag{51}$$

as can be proved by repeating the arguments presented in Sec. 5. Taking (51) into consideration, we obtain

$$\sigma(v) \sim S\frac{|2\alpha - \beta|}{|\varepsilon' - \varepsilon - \beta v + 2\alpha - \beta|}. \tag{52}$$

The $\sigma(v)$ dependence is generally speaking complicated, but it is possible to single out two asymptotic cases that correspond to two stages of the excitation.

In the first stage of the excitation, the terms linear in v and contained in the expression for σ are larger than the quadratic ones. The appearance of linear terms is connected with the fact that $\varepsilon = \Delta \cdot v$, where Δ is the detuning of the laser frequency from the frequency of the 0–1 transition. In this case

$$\sigma = \sigma_1/\sqrt{n}, \tag{53}$$

where σ_1 is a certain absorption cross section, which is a characteristic of the molecule, in the first stage of the excitation. In the second stage of the excitation the quadratic terms are much larger than the linear ones; therefore

$$\sigma = \sigma_2/n, \tag{54}$$

where σ_2 is the absorption cross section in the second stage.

Substituting (53) and (54) in (50), we find that in the first stage

$$n = (\sigma_1 W)^{2/3}. \tag{55}$$

where $W = \int_0^\tau I\,dt$ is the energy density of the pulse; τ is the duration of the pulse. In the second stage

$$n = (\sigma_2 W)^{1/2}. \tag{56}$$

Thus, the obtained expressions (55) and (56) show that the energy absorbed by the molecules is determined, for a fixed laser frequency, by the energy density of the laser pulse, and at low energy densities, when the number of absorbed photons is small, we have ($n \sim W^{2/3}$), while at large energy densities $n \sim W^{1/2}$.

The number of absorbed photons is largest in the case when the level density in the vicinity of the excited states is maximal. This takes place if, at a fixed laser-pulse energy density, the laser frequency is chosen such that the excited states have an energy satisfying the condition

$$\varepsilon_2 < \varepsilon < \varepsilon_c. \tag{57}$$

In this case, for the states with energy $\varepsilon \to \varepsilon_2$ the sum of the squares of the dipole moments $S \to \infty$. This shows that the most optimal will be the laser frequency for which the excited states have an energy $\varepsilon \approx \varepsilon_2$.

7. A band structure is possessed by the quasicontinuum of any molecule that has degenerate vibrations. Examples are not only the molecules $XY_4(T_d)$ and $XY_6(O_h)$, but also, e.g., the planar molecules of the type $XY_3(D_{3h})$. Among the latter is included the molecule BCl_3. In experiments on collisionless dissociation of the gas BCl_3 [14], the mode ν_3 of symmetry E was resonantly excited. The levels of this mode, which are degenerate in the harmonic approximation, are split by the anharmonicity and also form a quasicontinuum band structure.

The formation of bands can take place also in less symmetrical molecules on account of the random degeneracy of the oscillations. An example can be the molecule C_2H_4. The two atoms in the C_2H_4 molecule can be approximately regarded as one compound atom. In this approximation the molecule C_2H_4 has a fourfold symmetry axis and should be a symmetrical top. Indeed, with very good accuracy the molecule C_2H_4 is a symmetrical top [15]. It therefore has normal vibrations that are close in frequency and are active in the IR region, namely, ν_7 and ν_9. It is precisely upon excitation of these vibrations that one observes collisionless dissociation of the gas C_2H_4 [16].

Notice should be taken of one more possibility of band formation, namely the splitting, by anharmonicity, of levels of degenerate compound vibrations. Assume we have a compound vibration $\omega_{com} = \Sigma m_i \omega_i$, where m_i are positive integers and ω_i are the frequencies of the natural vibrations. If Σm_i is equal to 2-3, then the compound vibration has a noticeable dipole moment. The degeneracy of the compound vibration is equal to the product of the multiplicities of the degeneracy of the vibrations $m_i \omega_i$ that produce it, and can be very high. We consider a compound vibration with degeneracy multiplicity $M \gg 3$. Levels that are degenerate in the harmonic approximation, namely $v\hbar\omega_{com}$, where v is the vibrational quantum number, are split by the anharmonicity and form a band. The dipole moment of the transition between the levels of the neighboring bands is of the order of magnitude of the dipole moment of the main transitions of the compound vibration. The width of the bands increases in proportion to v^2, and the number of levels in the bands increases in proportion to v^{M-1}. Therefore, the average distance between the levels of one band in the case $M > 3$ decreases as v^{3-M}, or remains constant at $M = 3$. If the bands of the compound vibrations overlap the corresponding harmonic values of the energy, then resonant excitation of the molecules at the frequency of the compound vibrations is possible up to the dissociation levels.

8. In conclusion, let us formulate the main results of the present paper.

We determined the form of the vibrational Hamiltonian of the triply degenerate modes of molecules of the type $XY_4(T_d)$ and $XY_6(O_h)$. A method was developed for determining the energy eigenvalues of the degenerate vibrations with the aid of generating functions. Analytic expressions were obtained to describe the anharmonic splitting of the lower vibrational levels.

The specific singularities of the spectra of the high-lying vibrational states were considered and it was shown that the quasicontinuum of the vibrational states of polyatomic molecules has a band structure.

Approximate analytic expressions describing the energy position of the bands of degenerate vibrations of molecules of the type XY_4 and XY_6 were obtained. A criterion was derived for the nonaccumulation of the detunings that result from the anharmonicity of the vibrations. The distribution of level density in the bands was obtained. An approximate analytic expression describing the distribution of the strengths of the dipole moments of the transition between bands was obtained. The kinetics of the band excitation was analyzed. Approximate expressions describing the kinetics of the excitation were obtained.

The author thanks Professor N. V. Karlov for suggesting the problem and for interest in the work. He is grateful to S. S. Alimpiev and V. M. Akulin for helpful discussions.

LITERATURE CITED

1. N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. S. Richardson, Can. J. Phys., 51, 1281-1294 (1973).
2. R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Pis'ma Zh. Eksp. Teor. Fiz., 20, 597-600 (1974).
3. G. A. Askar'yan, Zh. Eksp. Teor. Fiz., 46, 403-413 (1964); 48, 666-675 (1965).
4. F. V. Bunkin, R. V. Karapetyan, and A. M. Prokhorov, ibid., 47, 216-225 (1964).
5. F. V. Bunkin and I. I. Tugov, ibid., 58, 1987-1998 (1970).
6. V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and L. A. Shelepin, ibid., 69, 836-841 (1975).
7. N. Bloembergen, Opt. Commun., 15, 416-420 (1975).
8. V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and B. G. Sartakov, in: Abstracts of Papers, 8th All-Union Conf. on Coherent and Nonlinear Optics, Vol. II, Tbilisi, Metsnereba (1976), p. 112.
9. V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and B. G. Sartakov, Zh. Eksp. Teor. Fiz., 72, 88-96 (1977).
10. C. D. Cantrell and H. W. Galbraith, Opt. Commun., 18, 513-517 (1976).
11. C. C. Jensen, W. B. Person, B. J. Krohn, and J. Overend, ibid., 20, 275-279 (1977).
12. W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev., 56, 895-907, 1097-1112 (1939).
13. L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Nonrelativistic Theory, Pergamon (1978).

14. J. I. Steinfeld, I. Burak, D. G. Sutton, and A. V. Novak, J. Chem. Phys., 52, 5421-5432 (1970).
15. R. V. Ambartsumyan, V. S. Dolzhikov, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Zh. Eksp. Teor. Fiz., 69, 72-84 (1975).
16. G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 3, Van Nostrand (1966).
17. O. N. Avatkov, V. N. Bagratashvili, I. N. Knyazev, et al., Kvantovaya Elektron. (Moscow), 4, 741-752 (1977).