Gamma-transition spectrum of a nucleus in a symmetric polyatomic molecule

V. S. Letokhov and V. G. Minogin

Institute of Spectroscopy, USSR Academy of Sciences
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The γ spectrum of a nucleus at the center of mass of a polyatomic molecule as affected by the change in the vibrational state of the molecule incident to the emission or absorption of a γ quantum by the nucleus is discussed. Formulas are derived for vibrational-nuclear transition probabilities in symmetric molecules of types XY_2 ($D_{\infty h}$), XY_3 (D_{3h}), XY_4 (T_d), XY_3Z_2 (D_{3h}), and XY_6 (O_h), and for the intensities of the components of the corresponding γ-ray emission and absorption spectra.

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1. INTRODUCTION. FORMULATION OF THE PROBLEM

As is known, the spectrum of γ transitions of a nucleus in an atom or molecule has a discrete structure associated with electronic transitions (for nuclei in atoms) and electronic-vibrational-rotational transitions (for nuclei in molecules).[1,2] The considerable interest that has arisen in the discrete γ spectra of nuclei in atoms or molecules is mainly due to the fact that this spectrum can be altered by laser irradiation, which excites the atomic or molecular levels from which quantum transitions take place as a result of recoil. Thus, in atomic and molecular gases one can compensate the shift of γ-ray emission and absorption lines by producing additional components of the γ spectrum close to these emission and absorption lines,[2,3] and in the case of a low-pressure gas one can produce narrow frequency-tunable γ resonances within a Doppler broadened γ line.[4]

The calculations reported in[2,3] showed that the components of the γ spectrum associated with electronic transitions have very low intensities in both atoms and molecules, the corresponding transition probabilities being proportional to the square of the ratio m_e/M, where m_e is the electron mass and M is the mass of the atom (or molecule). For this reason the γ spectra of nuclei in molecules associated with molecular vibrational-rotational transitions resulting from recoil are of especial interest.

Of course, even if the γ spectrum of a nucleus in a molecule is not associated with any change in the electronic state of the molecule, it must, generally speaking, be associated with molecular vibrational-rotational transitions because of the transfer to the molecule, simultaneously with the absorption or emission of a γ-ray photon, of both momentum and angular momentum, which entails a simultaneous change in both the vibrational and rotational states of the molecule. For example, in the case of a γ-active nucleus in a diatomic molecule, it is impossible to treat the vibrational-nuclear and rotational-nuclear transitions separately, even in the zeroth approximation.[3] This situation obviously obtains whenever the γ-active nucleus does not lie at the center of mass of the molecule. When the γ-active nucleus does lie at the center of mass of the

molecule, however, one can treat the vibrational transitions alone, neglecting the rotational transitions. This approximation is of especial importance for molecules in which the position of the γ-active nucleus at the molecular center of mass is not accidental, but is due to the symmetry of the molecule.

For experimental purposes it is important to know the probabilities for molecular quantum transitions due to recoil, for these determine both the change in the molecular state and the structure of the γ spectrum of the nucleus in the molecule. The foundations for a general theory of the emission and absorption of γ radiation by nuclei in symmetric polyatomic molecules were developed in[1], where the case of a molecule of type XY_2 was treated without allowance for the degeneracy of the vibrations. The purpose of the present paper is to discuss the γ spectra of nuclei at the centers of mass of the symmetric polyatomic molecules that are of the greatest experimental interest, and to derive specific formulas for the vibrational-nuclear transition probabilities with allowance for the symmetry of the normal vibrations as well as for the degeneracy of the vibrational levels that is inevitable in the case of polyatomic molecules. In what follows we shall discuss only a few frequently encountered types of molecules, namely: triatomic molecules of type XY_2 ($D_{\infty h}$), tetratomic molecules of type XY_3(D_{3h}), pentatomic molecules of type XY_4(T_d), hexatomic molecules of type XY_3Z_2(D_{3h}), and heptatomic molecules of type XY_6(O_h).

2. GENERAL RELATIONSHIPS. EXCLUSION OF ROTATIONS

In the zeroth approximation in the molecular Hamiltonian, the probability for a molecule having a γ-active nucleus[1] at its center of mass to execute a transition from state a to state b as a result of recoil incident to the emission or absorption of a γ quantum is determined by the matrix element[5]

$$M(b, a) = \langle b | \exp(-i\mathbf{k}_\gamma \mathbf{u}) | a \rangle, \qquad (1)$$

in which a and b are sets of quantum numbers specifying the vibrational and rotational states of the molecule before and after the interaction, $\mathbf{k}_\gamma$ is the wave vector of γ quantum, and $\mathbf{u}$ is the displacement vector of the nu-

cleus from its equilibrium position at the center of mass of the molecule, referred to a coordinate system fixed in space. The energy E_γ of the emitted or absorbed photon is determined by the change $E_b - E_a$ in the internal energy of the molecule, and in the non-relativistic approximation it is given by

$$E_\gamma = E_\gamma^0 \pm R + \hbar k_\gamma v \pm (E_b - E_a),\qquad(2)$$

in which E_γ^0 is the nuclear transition energy, $R = (E_\gamma^0)^2/2Mc^2$ is the recoil energy of the molecule (M is the molecular mass), v is the velocity of the molecule before the interaction, and the plus and minus signs correspond to γ-ray absorption and emission.

Let us determine the average energies expended in exciting molecular vibrations and rotations when the nucleus at the center of mass of the molecule emits or absorbs a γ ray.

If we neglect the molecular rotations and assume that a coordinate system fixed to the molecule is also fixed in space, we can express the displacement u of the γ-active nucleus in terms of the normal coordinates of the molecule. If we also assume for simplicity that only one nondegenerate normal vibration is excited (vibrational quantum $\hbar\omega$) and that the molecule was initially in the vibrational level $v_a = 0$, we can use the results obtained in[1] for the probabilities $P(v_b, v_a)$ for molecular vibrational transitions due to recoil. The average energy expended in exciting one normal vibration of the molecule is given by the formula

$$\bar{E}_{vit} = \sum_{r=0}^{\infty} \hbar\omega(v+{}^1\!/_2)\bar{P}(v,0) - \hbar\omega/2 = \sum_{v=0}^{\infty} \hbar\omega(v+{}^1\!/_2)P(v,0) - \hbar\omega/2$$

$$= \sum_{v=0} \hbar\omega(v+{}^1\!/_2)\frac{z^v}{v!}e^{-z} - \frac{\hbar\omega}{2} = \frac{1}{2}R\left(\frac{M-m}{m}\right),\qquad(3)$$

in which m is the mass of the γ-active nucleus, M is the mass of the molecule, $z = (R/\hbar\omega)(M-m)/m)\cos^2\vartheta$, where ϑ is the angle between the displacement vector of the nucleus and the wave vector of the γ quantum, and the bar indicates averaging over the molecular orientation or, what is the same thing, over the angle ϑ.

In determining the average energy expended in exciting molecular rotations, we obviously cannot neglect the molecular vibrations, since it is precisely on account of them that the angular momentum $L = k_\gamma u \sin\vartheta$ transferred to the molecule by the γ quantum does not vanish. We assume as before that the nucleus is coupled to only one nondegenerate normal vibration and that the vibrational state of the molecule does not change ($v_a = v_b = 0$); then the average energy expended in exciting rotations is the average over the vibrations of the rotational energy of the molecule:

$$\bar{E}_{rot} = \overline{\langle BL^2\rangle} = Bk_\gamma^2\langle u^2\rangle\overline{\sin^2\vartheta} = {}^1\!/_2R(B/\hbar\omega)[(M-m)/m].\qquad(4)$$

Here B is the rotational constant of the molecule and, as before, we have averaged over the molecular orientation. Of course the assumptions made above that only one molecular normal vibration is excited and that the

molecule was initially in the vibrational ground state are not important and cannot affect the order of magnitude of the results obtained in Eqs. (3) and (4). Thus, it turns out that

$$\bar{E}_{rot}/\bar{E}_{vib} \sim B/\hbar\omega,\qquad(5)$$

i.e., when a nucleus at the center of mass of a polyatomic molecule emits or absorbs a γ ray, the ratio of the average energy expended in exciting molecular rotations to that expended in exciting molecular vibrations is equal in order of magnitude to the ratio of the energy of a rotational quantum to that of a vibrational quantum. Since typical values of $B/\hbar\omega$ for polyatomic molecules lie in or near the range 10^{-4}–10^{-2}, it is a good approximation to neglect the molecular rotations and treat the γ spectrum of a nucleus at the center of mass of a polyatomic molecule as the spectrum of vibrational-nuclear transitions.

As was mentioned above, neglecting the molecular rotations means identifying a coordinate system fixed to the molecule with a coordinate system fixed in space. Hence the displacement u of the γ-active nucleus can be expressed in terms of the normal coordinates $Q_{s\sigma}$ of the molecule:

$$u = \frac{1}{\sqrt{m}}\sum_{s\sigma} b_{s\sigma}Q_{s\sigma},\qquad(6)$$

where m is the mass of the γ-active nucleus, while the components of the nuclear displacement vector $b_{s\sigma}$ representing the displacement of the nucleus due to the σ component of the s-th normal vibration of the molecule are elements of the matrix b[6] that effects the orthogonal transformation of the normal-coordinate matrix Q of the molecule to the matrix q of the mass-weighted Cartesian components of the nuclear displacements. In accordance with (6), matrix element (1) can be written as a product of matrix elements—one for each normal vibration of the molecule that contributes to the displacement of the γ-active nucleus:

$$M(b,a) = \prod_s \left\langle v_s^b \left| \prod_\sigma \exp(-ik_\gamma b_{s\sigma}Q_{s\sigma}/\sqrt{m}) \right| v_s^a \right\rangle.\qquad(7)$$

We note that if the normal vibration s' does not contribute to the displacement of the γ-active nucleus (e.g., if it is the fully symmetric vibration of a molecule having the γ-active nucleus at the center of symmetry) the corresponding matrix element vanishes except for transitions in which the vibrational quantum number of the corresponding normal vibration of the molecule does not change: $v_{s'}^a = v_{s'}^b$

In the approximation we are considering, neglecting the molecular rotations also means neglecting the rotations associated with degenerate vibrations, Hence the molecular wave function should be written in the form

$$|v_s\rangle = \Phi_{v_s}(Q_s)\qquad(8)$$

for a nondegenerate vibration, in the form

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$$|v_s\rangle = (v_s+1)^{-1/2} \sum_{v_{s\sigma_1}, v_{s\sigma_2}} \Phi_{v_{s\sigma_1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \qquad (9)$$

(with $v_{s\sigma_1} + v_{s\sigma_2} = v_s$) for a twofold degenerate vibration, and in the form

$$|v_s\rangle = \left(\frac{2}{(v_s+1)(v_s+2)} \right)^{1/2} \sum_{v_{s\sigma_1}, v_{s\sigma_2}, v_{s\sigma_3}} \Phi_{v_{s\sigma_1}}(Q_{s\sigma_1}) \Phi_{v_{s\sigma_2}}(Q_{s\sigma_2}) \Phi_{v_{s\sigma_3}}(Q_{s\sigma_3})$$

(10)

(with $v_{s\sigma_1} + v_{s\sigma_2} + v_{s\sigma_3} = v_s$) for a threefold degenerate vibration; here the $\Phi_{v_{s\sigma}}(Q_{s\sigma})$ are linear harmonic oscillator wave functions. Since explicit expressions are available for the wave functions $|v_s^a\rangle$ and $|v_s^b\rangle$, the calculation of matrix element (7) reduces to the calculation of matrix elements for each component σ of the normal vibration. These matrix elements have been calculated in,[3] but in view of their importance for subsequent applications, we give an expression for them in terms of associated Laguerre polynomials:

$$\langle \Phi_{v'_{s\sigma}}(Q_{s\sigma}) | \exp\{-i\mathbf{k}_\gamma \mathbf{b}_{s\sigma} Q_{s\sigma} m^{-1/2}\} | \Phi_{v_{s\sigma}}(Q_{s\sigma}) \rangle$$

$$= \left(\frac{v_{s\sigma}a!}{v_{s\sigma}b!} \right)^{1/2} \exp\left\{ -\frac{1}{2} z_{s\sigma} \cos^2 \alpha_{s\sigma} \right\} z_{s\sigma}^{\gamma/2} \cos^{\gamma'} \alpha_{s\sigma}$$

$$\times L_{v_{s\sigma}}^{\gamma'}(z_{s\sigma} \cos^2 \alpha_{s\sigma}) \cdot \begin{cases} (-1)^{\gamma'/2}, & \gamma'=2m \\ -i \cdot (-1)^{(\gamma'-1)/2}, & \gamma'=2m+1 \end{cases}$$

$$\gamma' = v_{s\sigma}^b - v_{s\sigma}^a.$$

(11)

Here $z_{s\sigma} = (R/\hbar\omega_s)(M/m) b_{s\sigma}^2$, $\alpha_{s\sigma}$ is the angle between the vector $\mathbf{k}_\gamma$ and the direction of the displacement of the nucleus due to the σ component of the s-th normal vibration of the molecule, and $m = 0, 1, 2, \ldots$.

In accordance with (11), the vibrational-nuclear transition probabilities are entirely determined by the parameters $z_{s\sigma}$. The main difficulty in calculating these parameters comes from the necessity of determining the $b_{s\sigma}$—the normalized displacements of the γ-active nucleus from its equilibrium position. When the molecule has only one normal vibration of a given symmetry type, the corresponding quantities $b_{s\sigma}$ can be easily determined from the molecular symmetry, the Eckart conditions, and the normalization condition, but when there are several normal vibrations of the same symmetry type one can evaluate the $b_{s\sigma}$, generally speaking, only if the constants of the secular equation $|GF - \lambda E| = 0$ of the molecule are known.[7] In discussing specific molecular types below, we shall determine the $b_{s\sigma}$ only for those vibrations that are the only ones of their symmetry type. Expressions for the remaining $b_{s\sigma}$ in terms of the constants of the secular equation of the molecule—in particular, in terms of the Coriolis ζ constants—can be derived from the elements of the matrix l that effects the inverse transformation from the matrix q to the matrix Q, and by now such expressions have been tabulated for all molecular types of practical interest. Because the transformation effected by the matrix l is orthogonal, the components $b_{s\sigma}^x$, $b_{s\sigma}^y$, and $b_{s\sigma}^z$ of $\mathbf{b}_{s\sigma}$ are elements of the transposed matrix l^+.

Finally, the energy of the absorbed or emitted γ quantum is given in the present approximation by Eq. (2) with

$$E_b - E_a = \sum_s \hbar\omega_s (v_s^b - v_s^a), \qquad (12)$$

where the v_s are the vibrational quantum numbers of only those normal vibrations that contribute to the displacement of the γ-active nucleus.

3. TRIATOMIC MOLECULE OF TYPE XY$_2$

The linear symmetric triatomic molecule of type XY$_2$ belonging to the point group $D_{\infty h}$ is the only triatomic molecule that satisfies condition (5) and is the only one of the symmetric polyatomic molecules considered here for which all the parameters $z_{s\sigma}$ can be evaluated from the molecular symmetry alone. We choose a coordinate system with the z axis coinciding with the C_∞ axis of the molecule and the origin at the equilibrium position of nucleus X. Then the displacement of the central nucleus along the z axis will be due to the antisymmetric vibration ν_3 of symmetry type Σ_u^+, and the displacement in the xy plane, to the twofold degenerate bending vibration of symmetry type Π_u; as was noted above, the fully symmetric vibration ν_1 of symmetry type Σ_g^+ does not contribute to the displacement of nucleus X. Thus, the displacements along the coordinate axes are

$$x = m_X^{-1/2} b_{2a}^x Q_{2a}, \quad y = m_X^{-1/2} b_{2b}^y Q_{2b}, \quad z = m_X^{-1/2} b_3^z Q_3, \qquad (13)$$

where, in accordance with the symmetry of the molecule and the normalization condition,

$$b_{2a}^x = b_{2b}^y = b_3^z = b = (2m_Y/M)^{1/2}. \qquad (14)$$

In these formulas m_X and m_Y are the masses of nuclei X and Y. According to (14), the vibrational-nuclear transition probabilities will depend only on the two parameters

$$z_2 = (R/\hbar\omega_2)(2m_Y/m_X), \quad z_3 = (R/\hbar\omega_3)(2m_Y/m_X). \qquad (15)$$

As an example, let us calculate the transition probability from the state $v_2^a = 0$, $v_3^b = 0$ to the state $v_2^b = 1$, $v_3^b = 0$. According to Eqs. (8) and (9), the wave functions for these states have the form

$$|0_2\rangle = \Phi_0(Q_{2a}) \Phi_0(Q_{2b}),$$

$$|1_2\rangle = \frac{1}{\sqrt{2}} [\Phi_1(Q_{2a}) \Phi_0(Q_{2b}) + \Phi_0(Q_{2a}) \Phi_1(Q_{2b})], \qquad (16)$$

$$|0_3\rangle = \Phi_0(Q_3).$$

According to (11), matrix element (7) is given by

$$M(10,00) = \langle 1_2 | \exp\{-ik_{\gamma x} b Q_{2a} m_X^{-1/2}\}$$

$$\times \exp\{-ik_{\gamma y} b Q_{2b} m_X^{-1/2}\} |0_2\rangle \langle 0_3| \exp\{-ik_{\gamma z} b Q_3 m_X^{-1/2}\} |0_3\rangle$$

$$= -i(z_2/2)^{1/2} (\cos\alpha_x + \cos\alpha_y) \exp\{-1/2(z_2 \cos^2\alpha_x + z_2 \cos^2\alpha_y + z_3 \cos^2\alpha_z)\}.$$

(17)

Using the identity $\cos^2\alpha_x + \cos^2\alpha_y + \cos^2\alpha_z = 1$, we write the square of the modulus of the matrix element in the form

$$|M(10,00)|^2 = 1/2 z_2 (\cos\alpha_x + \cos\alpha_y)^2 e^{-z_2} \exp\{(z_2 - z_3) \cos^2\alpha_z\}. \qquad (18)$$

It is convenient to do the angular average in spherical

TABLE 1. Vibrational-nuclear transition probabilities for molecules of type $XY_2(D_{\infty h})$.

Vibrational transition $v_2{}^a,\ v_3{}^a - v_2{}^b,\ v_3{}^b$	$\bar{P}(v_2{}^b v_3{}^b,\ v_2{}^a v_3{}^a)\exp z_2$
0,0—0,0	$_1F_1(^1/_2,\ ^3/_2,\ z_2 - z_3)$
0,0—1,0	$_1F_1(^1/_2,\ ^5/_2,\ z_2 - z_3)\,z_2/3$
0,0—0,1	$_1F_1(^3/_2,\ ^5/_2,\ z_2 - z_3)\,z_3/3$
0,0—2,0	$_1F_1(^1/_2,\ ^7/_2,\ z_2 - z_3)\,z_2{}^2/9$
0,0—0,2	$_1F_1(^5/_2,\ ^7/_2,\ z_2 - z_3)\,z_3{}^2/10$
1,0—1,0	$[\bar{P}(00,00) - 2\bar{P}(10,00) + {}^9/_5\,\bar{P}(20,00)]\,e^{z_2}$
1,0—0,1	$_1F_1(^3/_2,\ ^7/_2,\ z_2 - z_3)\,z_2 z_3/15$
0,1—0,1	$[\bar{P}(00,00) - 2\bar{P}(02,00) - 2\bar{P}(01,00)]\,e^{z_2}$

coordinates, writing

$$\cos\alpha_x = \sin\vartheta\cos\varphi, \quad \cos\alpha_y = \sin\vartheta\sin\varphi, \quad \cos\alpha_z = \cos\vartheta.$$

After integrating we obtain the following result:

$$\bar{P}(10,00) = \frac{1}{4\pi}\int |M(10,00)|^2 \sin\vartheta\,d\vartheta\,d\varphi = \frac{z_2}{3}e^{-z_2}\,{}_1F_1(^1/_2,\ ^5/_2,\ z_2-z_3),$$

$$(19)$$

where $_1F_1(a,b,c)$ is the confluent hypergeometric function.

Table 1 gives the calculated vibrational-nuclear transition probabilities for molecules of type $XY_2(D_{\infty h})$ between states in which not more than one vibrational quantum is excited. Transition probabilities of this type that are not listed in the table can be obtained from the relations between the probabilities for direct and inverse transitions:

$$\bar{P}(v_2{}^b v_3{}^b,\ v_2{}^a v_3{}^a) = \bar{P}(v_2{}^a v_3{}^b,\ v_2{}^b v_3{}^a) = \bar{P}(v_2{}^b v_3{}^a,\ v_2{}^a v_3{}^b) = \bar{P}(v_2{}^a v_3{}^a,\ v_2{}^b v_3{}^b).$$

$$(20)$$

4. TETRATOMIC MOLECULES OF TYPE XY_3

The normal vibrations of a symmetric tetratomic molecule of type XY_3 (point group D_{3h}) are distributed in symmetry types as follows:

$$A_1' + A_2'' + 2E'. \tag{21}$$

We choose a coordinate system with the origin at the equilibrium position of nucleus X, the z axis along the C_3 axis of the molecule, and the x axis passing through the equilibrium position of one of the nuclei Y. In accordance with (21), only the bending vibration ν_2 of symmetry type A_2'' contributes to the displacement of nucleus X along the z axis, while the two twofold degenerate vibrations ν_3 and ν_4 of symmetry type E' determine the displacement in the xy plane. The components of the displacement u of nucleus X from its equilibrium position are

$$x = m_X^{-1/2}(b_{3a}{}^x Q_{3a} + b_{4a}{}^x Q_{4a}), \quad y = m_X^{-1/2}(b_{3b}{}^y Q_{3b} + b_{4b}{}^y Q_{4b}), \quad z = m_X^{-1/2} b_2{}^z Q_2. \tag{22}$$

Here only one element can be determined from the symmetry of the molecule and the normalizing condition:

$$b_2{}^z = (3m_Y/M)^{1/2}. \tag{23}$$

The vibrational-nuclear transition probabilities between states $v_2{}^a$, $v_3{}^a$, $v_4{}^a$ and $v_2{}^b$, $v_3{}^b$, $v_4{}^b$ will depend on the

five parameters

five parameters

$$z_2 = (R/\hbar\omega_2)\,(3m_Y/m_X),\quad z_{3a},\quad z_{3b},\quad z_{4a},\quad z_{4b}. \tag{24}$$

The calculated vibrational-nuclear transition probabilities between states in which not more than one vibrational quantum is excited are listed in Table 2. The calculation procedure is similar to that outlined in Eqs. (17)–(20). Transition probabilities that can be obtained from the listed ones by obvious permutation of the vibrational quantum numbers referring to a single normal vibration or, in accordance with the equivalence of the vibrations ν_3 and ν_4, by exchanging indices relating to these two vibrations, are not included in the table. It is obvious, for example, that

$$\bar{P}(001,001) = \bar{P}(010,010)\ (v_3 = 1 \to v_3 = 0.v_4 = 0 \to v_4 = 1, z_{3a} \to z_{4a}, z_{3b} \to z_{4b})$$

$$= \bar{P}(000,000) - 2\bar{P}(001.000)$$

$$+ \frac{2}{15\pi}e^{-z_4}\int_0^\pi {}_1F_1(3,\ ^7/_2,u)\,(z_{4a}^{1/2}\cos\varphi + z_{4b}^{1/2}\sin\varphi)^4\,d\varphi. \tag{25}$$

5. PENTATOMIC MOLECULES OF TYPE XY_4 AND HEPTATOMIC MOLECULES OF TYPE XY_6

Molecules of types XY_4 (point group T_d) and XY_6 (point group O_h) belong to groups of the cubic system and can be treated together. For molecules of both types, only the threefold degenerate normal vibrations ν_3 and ν_4 contribute to the displacement of nucleus X; these vibrations are of symmetry type F_2 for the XY_4 molecules and of symmetry type F_{1u} for the XY_6 molecules. We choose a coordinate system with its axes coinciding with the three rotation-reflection axes S_4; for the XY_4 molecules these are the S_4 axes of a tetrahedron, and for the XY_6 molecules, those of a cube. Then the displacement of nucleus X can be written in the form

TABLE 2. Vibrational-nuclear transition probabilities for molecules of type $XY_3(D_{3h})$.

Vibrational transition $v_2{}^a,\ v_3{}^a,\ v_4{}^a - v_2{}^b,\ v_3{}^b,\ v_4{}^b$	$\bar{P}(v_2{}^b v_3{}^b v_4{}^b,\ v_2{}^a v_3{}^a v_4{}^a)\exp z_2$
0,0,0—0,0,0	$\dfrac{1}{\pi}\displaystyle\int_0^\pi {}_1F_1(1,\ ^3/_2,\ u)\,d\varphi$
0,0,0—1,0,0	$\dfrac{z_2}{3\pi}\displaystyle\int_0^\pi {}_1F_1(1,\ ^5/_2,\ u)\,d\varphi$
0,0,0—0,1,0	$\dfrac{1}{3\pi}\displaystyle\int_0^\pi {}_1F_1(2,\ ^5/_2,\ u)\,(z_{3a}^{1/2}\cos\varphi + z_{3b}^{1/2}\sin\varphi)^2\,d\varphi$
0,0,0—2,0,0	$\dfrac{z_2{}^2}{10\pi}\displaystyle\int_0^\pi {}_1F_1(1,\ ^7/_2,\ u)\,d\varphi$
1,0,0—1,0,0	$[\bar{P}(000,000) - 2\bar{P}(100,000) + 2\bar{P}(200,000)]\,e^{z_2}$
1,0,0—0,1,0	$\dfrac{z_2}{15\pi}\displaystyle\int_0^\pi {}_1F_1(2,\ ^7/_2,\ u)\,(z_{3a}^{1/2}\cos\varphi + z_{3b}^{1/2}\sin\varphi)^2\,d\varphi$
0,1,0—0,1,0	$[\bar{P}(000,000) - 2\bar{P}(010,000)]e^{z_2} + \dfrac{2}{15\pi}\displaystyle\int_0^\pi {}_1F_1(3,\ ^7/_2,\ u)\,(z_{3a}^{1/2}\cos\varphi + z_{3b}^{1/2}\sin\varphi)^4\,d\varphi$
0,1,0—0,0,1	$\dfrac{2}{15\pi}\displaystyle\int_0^\pi {}_1F_1(3,\ ^7/_2,\ u)\,(z_{3a}^{1/2}\cos\varphi + z_{3b}^{1/2}\sin\varphi)^2 \cdot (z_{4a}^{1/2}\cos\varphi + z_{4b}^{1/2}\sin\varphi)^2\,d\varphi$

Note: Here $u = (z_2 - z_{3a} - z_{4a})\cos^2\varphi + (z_2 - z_{3b} - z_{4b})\sin^2\varphi$.

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TABLE 3. Vibrational-nuclear transition probabilities for molecules of types XY_4 (T_d) and XY_6 (O_h).

Vibrational transition $v_3{}^a, v_4{}^a - v_3{}^b, v_4{}^b$	$\bar{P}(v_3{}^b v_4{}^b, \ v_3{}^a v_4{}^a)$ $X \exp (z_3 + z_4)$
0,0—0,0	1
0,0—1,0	$1/3 z_3$
1,0—1,0	$1/5 z_3^2 - 2/3 z_3 + 1$
1,0—0,1	$1/5 z_3 z_4$

$$x = m_X^{-1/2}(b_{3a}{}^x Q_{3a} + b_{4a}{}^x Q_{4a}),$$
$$y = m_X^{-1/2}(b_{3b}{}^y Q_{3b} + b_{4b}{}^y Q_{4b}), \qquad (26)$$
$$z = m_X^{-1/2}(b_{3c}{}^z Q_{3c} + b_{4c}{}^z Q_{4c}).$$

for the molecules of both types, where, in accordance with the symmetry of the molecules, we have

$$b_{3a}{}^x = b_{3b}{}^y = b_{3c}{}^z = b_3, \qquad b_{4a}{}^x = b_{4b}{}^y = b_{4c}{}^z = b_4. \qquad (27)$$

Thus, for the molecules under consideration the vibrational-nuclear transition probabilities from the state $v_3{}^a$, $v_4{}^a$ to the state $v_3{}^b$, $v_4{}^b$ will depend only on the two parameters z_3 and z_4.

As an example, let us consider the calculation of $\bar{P}(10,00)$, i.e. the transition probability from the state $v_3 = 0$, $v_4 = 0$ to the state $v_3 = 1$, $v_4 = 0$. According to (10) the wave functions have the form

$$|0_a\rangle = \Phi_0(Q_{3a})\Phi_0(Q_{3b})\Phi_0(Q_{3c}),$$
$$|1_a\rangle = 3^{-1/2}[\Phi_1(Q_{3a})\Phi_0(Q_{3b})\Phi_0(Q_{3c})$$
$$+ \Phi_0(Q_{3a})\Phi_1(Q_{3b})\Phi_0(Q_{3c}) + \Phi_0(Q_{3a})\Phi_0(Q_{3b})\Phi_1(Q_{3c})], \qquad (28)$$
$$|0_b\rangle = \Phi_0(Q_{4a})\Phi_0(Q_{4b})\Phi_0(Q_{4c});$$

and according to (11), matrix element (7) is given by

$$M(10.00) = \langle 1_b| \exp\{-ik_{\gamma x} b_3 Q_{3a} m_X^{-1/2}\}$$
$$\times \exp\{-ik_{\gamma y} b_3 Q_{3b} m_X^{-1/2}\} \exp\{-ik_{\gamma z} b_3 Q_{3c} m_X^{-1/2}\}|0_a\rangle \langle 0_b| \exp\{-ik_{\gamma x} b_4 Q_{4a} m_X^{-1/2}\}$$
$$\times \exp\{-ik_{\gamma y} b_4 Q_{4b} m_X^{-1/2}\} \exp\{-ik_{\gamma z} b_4 Q_{4c} m_X^{-1/2}\}|0_b\rangle$$
$$= (z_3/3)^{1/2}(\cos\alpha_x + \cos\alpha_y + \cos\alpha_z)\exp[-(z_3 + z_4)/2]. \qquad (29)$$

Averaging over the angles is a trivial task because of the spherical symmetry, and we finally obtain

$$\times \frac{\bar{P}(10.00) = |\overline{M(10.00)}|^2 = 1/3 z_3 \exp\{-(z_3 + z_4)\}}{(\cos\alpha_x + \cos\alpha_y + \cos\alpha_z)^2 = 1/3 z_3 \exp\{-(z_3 + z_4)\}.} \qquad (30)$$

Table 3 gives the vibrational-nuclear transition probabilities between states in which not more than one vibrational quantum is excited. For brevity we have omitted transition probabilities $\bar{P}(v_3{}^b, v_4{}^b, v_3{}^a v_4{}^a)$ that can be obtained from others by substituting z_4 for z_3. For example, by the substitution $z_3 \to z_4$ we obtain $\bar{P}(01,00) = (1/3)z_4$. We have also omitted transition probabilities that can be obtained from the relations between the probabilities for direct and inverse transitions.

6. HEXATOMIC MOLECULES OF TYPE XY_3Z_2

The normal vibrations of a molecule of type XY_3Z_2 (point group D_{3h}) are distributed in symmetry types

as follows

$$2A_1' + 2A_2'' + 3E' + E''. \qquad (31)$$

The vibrations ν_3 and ν_4 of symmetry type A_2'' and the vibrations ν_5, ν_6, and ν_7 of symmetry type E' contribute to the displacement of nucleus X.[8] If we choose the coordinate system the same as we did for tetratomic molecules of type XY_3 we find that the vibrations ν_3 and ν_4 contribute to the displacement of X on the z axis (the corresponding normalized displacements being b_3^z and b_4^z) and the vibrations ν_5, ν_6, ν_7 contribute to the displacement of X in the xy plane (normalized displacements, b_{5a}^x, b_{5b}^y, b_{6a}^{xx}, b_{6b}^y, b_{7a}^x, and b_{7b}^y). The vibrational-nuclear transition probabilities will depend on eight parameters $z_{s\sigma}$, none of which can be determined unless the constants of the secular equation of the molecule are known. We shall not tabulate the vibrational-nuclear transition probabilities for this molecule because of the large amount of space that would be required. In fact, only three of the vibrational quantum numbers remain unchanged and the transition probabilities depend on the remaining five: ν_3, ν_4, ν_5, ν_6, and ν_7. Of course the calculation of the transition probabilities is similar to the corresponding calculation for XY_3 molecules and, for example, the transition probability $\bar{P}(00000, 00000)$ can be obtained from the $\bar{P}(000, 000)$ of Table 2 by simply substituting $z_3 + z_4$ for z_2, $z_{5a} + z_{6a} + z_{7a}$ for $z_{3a} + z_{4a}$, and $z_{5b} + z_{6b} + z_{7b}$ for $z_{3b} + z_{4b}$.

We note that the tables represent three possible types of γ-ray spectra for nuclei at the centers of mass of symmetric polyatomic molecules that can arise in the vibrational-nuclear transition approximation on averaging over the molecular orientation. For spherical top molecules the averaged transition probabilities are given by polynomials in the $z_{s\sigma}$; for linear molecules, by confluent hypergeometric functions; and for symmetric top molecules, by definite integrals of confluent hypergeometric functions.

7. VIBRATIONAL TRANSITION PROBABILITIES FOR OsO$_4$

As an example of the use of the formulas obtained above, let us consider the probabilities for vibrational transitions of the ^{188}Os^{16}O$_4$ molecule (point group T_d) incident to the emission or absorption of an $E_\gamma^0 = 155$ keV photon by the ^{188}Os nucleus. Preliminary estimates[9] indicate that this molecule may prove to be of great interest for the experimental observation of vibrational-nuclear γ spectra, and in particular, for observation of the modulation of the Os γ radiation incident to the excitation of OsO$_4$ vibrations by the radiation from a continuous CO$_2$ laser.[10]

The matrix l for an XY_4 molecule belonging to the point group T_d can be taken, for example, from.[11] Then from the expressions for z_3 and z_4 in terms of the elements of the transposed matrix $l^T = b$, we obtain

$$z_3 = 4c^2 \frac{R}{\hbar\omega_3}\frac{m_Y}{m_X}, \qquad z_4 = 4s^2 \frac{R}{\hbar\omega_4}\frac{m_Y}{m_X}, \qquad (32)$$

in which c and s are functions of the molecular force

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constants that are determined in[11]. Since we need only the absolute values of c and s to evaluate z_3 and z_4, we can use the following expressions for these functions in terms of the Coriolis constants ζ_3 and ζ_4:

$$c^2 = \tfrac{2}{3}(2\zeta_3 + \zeta_4), \quad s^2 = \tfrac{2}{3}(\zeta_3 + 2\zeta_4). \tag{33}$$

Noting that we have $R = 0.051$ eV for the recoil energy and assuming the parameter values $\omega_3 = 960$ cm^{-1}, $\omega_4 = 329$ cm^{-1}, $\zeta_3 = 0.068$, and $\zeta_4 = 0.432$ in accordance with[12], we find $z_3 = 0.054$ and $z_4 = 0.260$. Then using Table 3 we obtain the following values for the first few transition probabilities:

$$\bar{P}(00,00) = 0.731, \quad \bar{P}(10,00) = 0.013, \quad \bar{P}(01,00) = 0.063,$$

$$\bar{P}(10,10) = 0.704, \quad P(01,01) = 0.614. \tag{34}$$

8. CONCLUSION. INTENSITIES IN THE γ SPECTRUM

The vibrational-nuclear transition probabilities discussed above directly determine the intensities of the components of the γ spectrum of a nucleus in a molecule. In the case of a single emission line centered at

$$E_\gamma^e = E_\gamma^0 - R - \sum_s \hbar\omega_s \Delta_s \tag{35}$$

($\Delta_s = v_s^b - v_s^a$ is the change in the vibrational quantum number of the s-th normal vibration), the line shape, i.e. the number of photons of energy E_γ emitted per unit time in the energy interval dE_γ, will be given by the obvious formula

$$w(E_\gamma) = \frac{\Gamma_\gamma}{\sqrt{\pi}\,\Delta E_D} \exp\left\{-\left(\frac{E_\gamma - E_\gamma^e}{\Delta E_D}\right)^2\right\} \sum_{v_s^a} n_{v^a} \bar{P}(v_s^a + \Delta_s, v_s^a), \tag{36}$$

in which Γ_γ is the half-width of the nuclear transition, $\Delta E_D = E_\gamma(2kT/Mc^2)^{1/2}$ is the Doppler half-width of the nuclear transition, and $n_{v_s^a}$ is the number of molecules that contain γ-active nuclei and are in the vibrational state specified by the quantum numbers v_s^a. For absorption spectra, the γ-ray absorption cross section per molecule (per γ-active nucleus) is of interest. The formula for it is a generalization of the well-known formula for the γ-ray absorption cross section of a free nucleus:

$$\sigma(E_\gamma) = \frac{\sqrt{\pi}}{2}\sigma_0 \frac{\Gamma_\gamma}{\Delta E_D} \sum_{v^a} \xi v_s^a \sum_{v^b} \bar{P}(v_s^b, v_s^a)\exp\left\{-\left(\frac{E_\gamma - E_\gamma^a}{\Delta E_D}\right)^2\right\}, \tag{37}$$

where σ_0 is the nuclear-transition cross section at maximum, ξv_s^a is the fraction of the molecules on the vibrational level v_s^a, and E_γ^a is the center of the absorption line corresponding to the transition of the molecule from state v_s^a to state v_s^b:

$$E_\gamma^a = E_\gamma^0 + R + \sum_s \hbar\omega_s(v_s^b - v_s^a). \tag{38}$$

Equations (36) and (37) together with the transition probabilities $\bar{P}(v_s^b, v_s^a)$ derived in this paper are sufficient for calculating γ-ray emission and absorption spectra of nuclei at the centers of mass of polyatomic molecules.

1)Here and below we shall for brevity refer to the nucleus that absorbs or emits γ radiation as the γ-active nucleus.

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