Spectrum of γ transitions of a nucleus in a diatomic molecule

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We discuss the γ spectrum of a nucleus in a diatomic molecule, due to change in the electronic-vibrational-rotational state of the molecule on emission or absorption of a γ ray by a nucleus of the molecule. It is shown that the components of the γ spectrum due to change in the vibrational-rotational state of the molecule are the most intense. The emission and absorption spectrum of the nucleus ^{127}I bound in the molecule H^{127}I is calculated, and the possibility of observing it is analyzed.

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1. INTRODUCTION. FORMULATION OF THE PROBLEM

It is well known that on emission or absorption of γ rays by the nuclei of atoms or molecules, the recoil by the nucleus leads to a change in the internal state of the atom or molecule. For example, on emission of γ rays with high energy the recoil can produce dissociation of the molecule (the Szilard-Chalmers effect[1]). On emission or absorption of a γ ray by a nucleus in a molecule, a change in the vibrational state occurs,[2] and in the case of a nucleus in an atom—a change in the electronic state of the atom occurs.[3,4] As a result of such vibrational-nuclear or electronic-nuclear γ transitions of the nucleus in a molecule or atom, the emission or absorption γ line acquires a complex structure. Near the γ lines of the free nucleus there arise satellites separated from the main line by a distance corresponding to the change in internal energy of the molecule or atom. The intensity of these satellites is determined by the probabilities of the corresponding vibrational-nuclear[2] or electronic-nuclear[3,4] transitions.

A fundamentally important possibility is that of changing the structure of the vibrational-nuclear or electronic-nuclear transitions as the result of excitation of levels of the molecule or atom by laser radiation. In this way it is possible to change the absorption or emission spectrum of the γ satellites due to quantum transitions with participation of the excited levels of the molecule or atom. In the case of gases at low pressure with a nonuniformly broadened absorption line in an electronic or vibrational transition, laser radiation can even change the shape of the Doppler-broadened emission or absorption γ lines.[5] This opens up the basic possibility of γ spectroscopy of nuclei in a gaseous medium without Doppler broadening. Therefore the study of the emission or absorption spectra of γ rays of nuclei bound in atoms or molecules presents considerable interest.

The probability of changing the internal state of an atom in a sudden action on the nucleus was apparently calculated for the first time by Migdal[6] in connection with the problem of collision of hydrogen atoms with neutrons. The change of the rotational state of a diatomic molecule as the result of the recoil effect has been considered by Podgoretskiĭ and Roĭzen.[7] The spectrum of vibrational nuclear γ transitions of a nucleus in a polyatomic molecule with the nucleus at the center of symmetry has been studied by Letokhov,[2] and the spectrum of electronic-nuclear γ transitions in an atom—by Letokhov and Ivanov.[3,4] The purpose of the present work is to consider the general case of change of the electronic-vibrational-rotational state of a diatomic molecule on emission or absorption of a γ ray and to calculate the structure of the spectrum of γ transitions. The solution of this problem cannot be obtained from previously solved problems[2-4,6,7] and requires individual discussion.

2. GENERAL RELATIONS

We shall assume for definiteness that the γ ray interacts with nucleus 1 of a diatomic molecule consisting of nuclei 1 and 2, and we shall designate by $\mathbf{r}_n$ the coordinates of the nucleons of nucleus 1 in the center-of-mass system of the molecule, by $\mathbf{r}_n'$ the coordinates of the nucleons in the center-of-mass system of nucleus 1, by $\mathbf{r}_e$ the coordinates of the electrons in the center-of-mass system of the molecule, and by $\mathbf{R}_1$ and $\mathbf{R}_2$ the coordinates of the center of mass of nuclei 1 and 2 with respect to the center of mass of the molecule. Let $\Psi(\mathbf{r}_n)$ be the wave function of the system of nucleons of nucleus 1; the wave function of the molecule, using the adiabatic approximation, we shall write in the form $\Psi(\mathbf{r}_e)\Psi(\mathbf{R}_1, \mathbf{R}_2)$, where $\Psi(\mathbf{r}_e)$ is the wave function of the electrons and $\Psi(\mathbf{R}_1, \mathbf{R}_2)$ is the wave function of the nuclei. The Hamiltonian of the interaction of γ radiation with the system of nucleons of nucleus 1 we shall express in a form convenient for further calculations: in terms of the coordinates of the nucleons $\mathbf{r}_n'$ in the center of mass system of nucleus 1:[2,8]

$$H(\mathbf{r}_n)=H(\mathbf{r}_n')\exp(-i\mathbf{k}_\gamma\mathbf{R}_1), \tag{1}$$

where $\mathbf{k}_\gamma$ is the wave vector of the γ ray.

In first-order perturbation theory the matrix element of the transition from the initial state a to the final state b, as a consequence of separation of the coordinates of the nucleons and nuclei in accordance with Eq. (1), can be written in the form of the product of two matrix elements, one of which corresponds to change of the internal state of the nucleus, and the other to change of the internal state of the molecule:

$$\begin{gathered}\langle\Psi_b^*(\mathbf{r}_n')\,|H(\mathbf{r}_n')|\,\Psi_a(\mathbf{r}_n')\rangle\\ \times\langle\Psi_b^*(\mathbf{r}_e)\,\Psi_b^*(\mathbf{R}_1,\mathbf{R}_2)\,|e^{-i\mathbf{k}_\gamma\mathbf{R}_1}|\,\Psi_a(\mathbf{r}_e)\,\Psi_a(\mathbf{R}_1,\mathbf{R}_2\rangle.\end{gathered} \tag{2}$$

Here the first factor is determined by the γ transition of the nucleus and to a good approximation does not depend on the internal state of the molecule. The second factor is the matrix element of the transition of the molecule from the initial state a to the final state b:

$$M_{ba}=\langle\Psi_b^*(\mathbf{r}_e)\,|\,\Psi_a(\mathbf{r}_e)\rangle$$
$$\times\langle\Psi_b^*(\mathbf{R}_1,\mathbf{R}_2)\,|\,e^{-i\mathbf{k}_\gamma\mathbf{R}_1}\,|\,\Psi_a(\mathbf{R}_1,\mathbf{R}_2)\rangle. \qquad (3)$$

It is evident that the retention in the matrix element of the separation into electronic and nuclear motions is a consequence of neglecting the nonadiabatic terms.

The expression presented (3) solves in general form the problem of the probabilities of change of the internal state of the molecule on emission or absorption of a γ ray by a nucleus of the molecule and determines the amplitudes of the respective γ satellites. In regard to their location, i.e., the energies E_γ of the emitted or absorbed γ ray, they are completely determined by conservation of energy and momentum, which in the nonrelativistic approximation have the form

$$\pm E_\gamma+E_a+{}^1/{}_2M\mathbf{v}_0^2=\pm E_\gamma^{(0)}+E_b+{}^1/{}_2M\mathbf{v}^2, \qquad (4)$$

$$M\mathbf{v}_0\pm\hbar\mathbf{k}_\gamma=M\mathbf{v}, \qquad (5)$$

where M is the mass of the molecule, $\mathbf{v}_0$ and $\mathbf{v}$ are the velocity of the molecule before and after interaction of the nucleus with the γ ray, $\mathbf{k}_\gamma$ is the wave vector of the γ ray, E_a and E_b are the internal energy of the molecule before and after the interaction, and $E_\gamma^{(0)}$ is the energy of the nuclear transition; the upper and lower signs here and subsequently refer respectively to absorption and emission of γ rays. From Eqs. (4) and (5) the energy of the γ satellite corresponding to the transition a → b is

$$E_\gamma=E_\gamma^{(0)}+\hbar\mathbf{k}_\gamma\mathbf{v}_0\pm R_{\gamma e}\pm(E_b-E_a), \qquad (6)$$

where $R_{\gamma e}=(E_\gamma^{(0)})^2/2Mc^2$ is the recoil energy of the molecule.

3. ELECTRONIC-NUCLEAR TRANSITIONS

As a result of the separation in the adiabatic approximation of transitions associated with change of the electronic and nuclear motions, it is possible to calculate individually the value of the matrix element on an electronic-nuclear transition

$$M_{ba}^{(e)}=\langle\Psi_b^*(\mathbf{r}_e')\,|\,\Psi_a(\mathbf{r}_e)\rangle; \qquad (7)$$

here the prime on the coordinate of the electrons in state b explicitly denotes the difference in the electronic coordinates before and after interaction of the nucleus with the γ ray, resulting from the change in location of the center of mass of the molecule. If the change in velocity of the center of mass of the molecule is $\Delta\mathbf{v}$, then the coordinate of the i-th electron in the center-of-mass system of the molecule after the interaction $\mathbf{r}_{ei}'$ can be expressed in terms of the coordinate $\mathbf{r}_{ei}$ in the center-of-mass system of the molecule before the interaction:

$$\mathbf{r}_{ei}'=\mathbf{r}_{ei}+\mathbf{R}(t), \qquad (8)$$

where $\mathbf{R}(t)=\Delta\mathbf{v}(t-t_0)$. Going over to the system of reference associated with the molecule before the interaction and taking into account Eq. (8), we express the wave function of the electrons $\Psi_b(\mathbf{r}_{ei}')$ in terms of the coordinates $\mathbf{r}_{ei}$.[9] We have

$$\Psi_b(\mathbf{r}_{ei}')=\Psi_b(\mathbf{r}_{ei})\exp\left[\frac{i}{\hbar}\sum_i m_e\Delta\mathbf{v}\left(\mathbf{r}_{ei}+\frac{1}{2}\mathbf{R}(t)\right)\right], \qquad (9)$$

or, using Eq. (5), we obtain

$$\Psi_b(\mathbf{r}_{ei}')=\Psi_b(\mathbf{r}_{ei})\exp\left(\pm i\frac{m_e}{M}\mathbf{k}_\gamma\sum_i\mathbf{r}_{ei}\right)\exp\left(\pm iZ\frac{m_e}{2M}\mathbf{k}_\gamma\mathbf{R}(t)\right), \qquad (10)$$

where Z is the number of electrons in the molecule.

Since in the matrix element (7) integration is carried out over the electronic coordinates and in the last analysis we are interested only in the square of the modulus of the matrix element, the last factor in Eq. (10) can be discarded. Having expressed the summation occurring in the argument of Eq. (10) in terms of the electronic dipole moment of the molecule

$$\mathbf{D}_e=e\sum_i\mathbf{r}_{ei},$$

we finally obtain

$$M_{ba}^{(e)}=\int\Psi_b^*(\mathbf{r}_{ei})\exp\left(\mp i\frac{m_e}{M}\frac{\mathbf{k}_\gamma\mathbf{D}_e}{e}\right)\Psi_a(\mathbf{r}_{ei})\,d^3r_{ei}. \qquad (11)$$

The only interesting γ rays are actually those with energy $E^{(0)}\sim$ 10 keV–10 MeV, associated with nuclear transitions either from isomeric states or from states excited as the result of nuclear reactions.[10] For these energies and for typical values of $M\sim 100$ amu and $D_e\sim 1$ D the argument of the exponential is $(m_e/M)(k_\gamma D_e/e)\sim 6\times10^{-6}$–$6\times10^{-3}\ll 1$. Expanding the exponential in series and retaining only the first two terms, we obtain from Eq. (11)

$$M_{ba}^{(e)}=\delta_{ba}\mp i\frac{m_e}{M}\frac{\mathbf{k}_\gamma\langle\mathbf{D}_e\rangle_{ba}}{e}, \qquad (12)$$

where $\langle D_e\rangle_{ba}$ is the matrix element of the electronic dipole moment of the molecule. The probability of electronic-nuclear transitions in the first nonzero approximation is

$$P_{ba}^{(e)}=\begin{cases}\left(\dfrac{m_e}{M}\right)^2\left(\dfrac{\mathbf{k}_\gamma\langle\mathbf{D}_e\rangle_{ba}}{e}\right)^2 & \text{for } a\neq b\\ 1 & \text{for } a=b\end{cases} \qquad (13)$$

The expression obtained (13) permits the following conclusions to be drawn. In the first place, it is evident that this equation must agree with the corresponding expression in the case of atoms[3,4] and must be valid for polyatomic molecules, since no specific assumptions about a diatomic molecule were made in its derivation. In the second place, the presence in the probability of electronic-nuclear transitions of the factor $(m_e/M)^2$ permits the statement that taking into account nonadiabatic terms (terms of the expansion in $(m_e/M)^{1/4}$) cannot significantly change the values of $P_{ba}^{(e)}$ calculated with neglect of the nonadiabatic terms. Finally, the low probability of electronic-nuclear transitions associated with change of the electronic state of the molecule permits the statement that dissociation of a molecule on emission or absorption of a γ ray by a nucleus of the molecule (the Szilard-Chalmers effect) occurs with overwhelming probability not as the result of excitation of electronic states of the molecule, but as the result of direct breaking of a bond of the molecule in the electronic ground state.

We note that in the case of a diatomic molecule with identical nuclei, reabsorption of the γ ray is possible.[11] The corresponding probability is $W\sim\sigma_\gamma/4\pi R^2\sim10^{-4}$–$10^{-5}$, where σ_γ is the cross section for γ absorption and R is the distance between nuclei.

It is clear that real interest is presented only by transitions between vibrational-rotational levels of the electronic ground state, including transitions to the continuum, accompanied by dissociation of the molecule. For such transitions the matrix element according to Eq. (3) is

$$M_{ba}=\langle\Psi_b^*(\mathbf{R}_1,\mathbf{R}_2)\,|\,e^{-i\mathbf{k}_\gamma\mathbf{R}_1}\,|\,\Psi_a(\mathbf{R}_1,\mathbf{R}_2)\rangle. \qquad (14)$$

We shall discuss systematically the matrix elements and probabilities of vibrational-nuclear and rotational-nuclear transitions in the harmonic-oscillator and rigid-rotator approximations, respectively.

4. VIBRATIONAL-NUCLEAR TRANSITIONS

In the harmonic-oscillator approximation for a diatomic molecule the wave function of the nuclei depends only on the change of the internuclear distance $R - R_0$,

$$\Psi(\mathbf{R}_1, \mathbf{R}_2)=(2^v v!\sqrt{\pi/\alpha})^{-1/2}\exp(-\alpha Q^2/2)H_v(\sqrt{\alpha}Q), \tag{15}$$

where $\alpha = \omega/\hbar$, $Q = (R - R_0)\sqrt{m}$, $m = m_1m_2/M$ is the reduced mass of the molecule, m_1 and m_2 are the masses of nuclei 1 and 2, and the coordinate of the center of mass of nucleus 1 relative to the center of mass of the molecule is determined by the expression

$$R_1=-\frac{m_2}{M}R=-\frac{m_2}{M}\left(R_0+\frac{Q}{\sqrt{m}}\right)=-\frac{m_2}{M}R_0-\left(\frac{m_2}{m_1M}\right)^{1/2}Q. \tag{16}$$

Substituting (15) and (16) into (14) and using the integrals from Ref. 12, we obtain

$$M_{v_b,v_a}=\exp\left(i\frac{m_2}{M}\mathrm{k}_\gamma\mathrm{R}_0\right)\left(\frac{v_a!}{v_b!}\right)^{1/2}\exp\left(-\frac{z_0\cos^2\vartheta}{2}\right)z_0^{(v_b-v_a)/2}\cos^{v_b-v_a}\vartheta$$
$$\times L_{v_a}^{v_b-v_a}(z_0\cos^2\vartheta)\begin{cases}(-1)^{(v_b-v_a)/2} & \text{for } v_b=v_a+2m\\ -i(-1)^{(v_b-v_a-1)/2} & \text{for } v_b=v_a+2m+1,\ m=0,1,2,\ldots\end{cases} \tag{17}$$

Here $z_0 = (R_{\mathrm{re}}/\hbar\omega)(m_2/m_1)$, and ϑ is the angle between $\mathbf{k}_\gamma$ and $\mathbf{R}$. Accordingly the probability of a transition from vibrational state v_a to vibrational state v_b is

$$P_{v_b,v_a}=\frac{v_a!}{v_b!}\exp(-z_0\cos^2\vartheta)(z_0\cos^2\vartheta)^{v_b-v_a}[L_{v_a}^{v_b-v_a}(z_0\cos^2\vartheta)]^2. \tag{18}$$

As a consequence of the distinguishing of the direction of the axis of the molecule in the approximation considered, the probability of a vibrational-nuclear transition P_{v_b,v_a} depends on the angle of emission ϑ of the γ ray relative to the axis of the molecule. Averaging over the directions of emission of the γ rays, we finally obtain for the probabilities averaged over angle the following expression:

$$\bar{P}_{v_b,v_a}=\frac{v_a!}{v_b!}(z_0)^{v_b-v_a}\int_0^1\exp(-z_0y^2)y^{2(v_b-v_a)}[L_{v_a}^{v_b-v_a}(z_0y^2)]^2\,dy. \tag{19}$$

For the γ-ray energy region of interest to us and for the energies of vibrational quanta $\hbar\omega \sim 10^2$–10^3 cm^{-1} characteristic of diatomic molecules, the parameter z_0 which determines the probability of vibrational nuclear transitions varies over a wide range: $z_0 \sim (4\times10^{-3}$–$4\times10^4)m_2/m_1$. The results of numerical calculations with Eq. (19) for $v_a = 0.1$ can be found in Ref. 2.

The energy of the γ satellite accompanying transition of the molecule from vibrational state v_a to state v_b according to Eq. (6) in the harmonic-oscillator approximation is

$$E_\gamma=E_\gamma^{(0)}+\hbar\mathrm{k}_\gamma\mathrm{v}_0\pm R_{0\gamma}\pm\hbar\omega(v_b-v_a). \tag{20}$$

5. ROTATIONAL-NUCLEAR TRANSITIONS

It is already evident from classical considerations that the change in the rotational state of a molecule on emission or absorption of a γ ray by a nucleus in the molecule is completely determined by the angular momentum transferred to the molecule

$$\hbar a_0=\hbar k_\gamma R_1^0=(E_\gamma^{(0)}/c)(m_2/M)R^0.$$

For the $E_\gamma^{(0)}$ indicated above and with the equilibrium internuclear distance $R^0 \sim 2$ Å typical of diatomic molecules, the angular momentum transferred to the molecule (in units of $\hbar$) is $a_0 \sim (10$–$10^4)m_2/M$, and thus for not too small m_2/M the change in the rotational state of the molecule can be significant.

In the rigid-rotator approximation the wave functions describing the motion of the nuclei of a molecule in a state with definite J and K are eigenfunctions of the angular momentum:

$$\Psi(\mathbf{R}_1, \mathbf{R}_2)=Y_{JK}(\vartheta,\varphi); \tag{21}$$

the angles ϑ and φ define in a spherical coordinate system the vector of relative location of the nuclei $\mathbf{R}^0 = \mathbf{R}_2^0 - \mathbf{R}_1^0$. Let ξ and η be the spherical coordinates of the wave vector of the γ ray $\mathbf{k}_\gamma$; then, taking into account that $\mathbf{R}_1^0 = -(m_2/M)\mathbf{R}^0$, we write the matrix element (14) in the form

$$M_{J_b,K_b;J_a,K_a}=\langle Y^*_{J_b,K_b}(\vartheta,\varphi)|\exp(ia_0\cos\gamma)|Y_{J_a,K_a}(\vartheta,\varphi)\rangle, \tag{22}$$

where γ is the angle between the vectors $\mathbf{R}^0(\vartheta, \varphi)$ and $\mathbf{k}_\gamma(\xi, \eta)$. For integration of Eq. (22) we expand the exponential in Bessel functions of half-integral order and use the superposition theorem for spherical harmonics:

$$\exp(ia_0\cos\gamma)=4\pi\sqrt{\frac{\pi}{2a_0}}\sum_{l=0}^{\infty}i^lJ_{l+1/2}(a_0)\sum_{m=-l}^{+l}Y_{lm}(\vartheta,\varphi)Y_{lm}^*(\xi,\eta). \tag{23}$$

Substitution of (23) into (22) permits integration to be carried out ϑ and φ and an expression to be obtained for the matrix element in terms of 3j symbols:

$$M_{J_b,K_b;J_a,K_a}=\sqrt{4\pi}[(2J_a+1)(2J_b+1)]^{1/2}(-1)^{K_b}$$
$$\times(\pi/2a_0)^{1/2}\sum_{l=|J_b-J_a|}^{J_a+J_b}i^l(2l+1)^{1/2}J_{l+1/2}(a_0)\begin{pmatrix}J_a & J_b & l\\ 0 & 0 & 0\end{pmatrix} \tag{24}$$
$$\times\sum_{m=-l}^{+l}Y_{lm}^*(\xi,\eta)\begin{pmatrix}J_a & J_b & l\\ K_a & -K_b & m\end{pmatrix}.$$

As a result of the fact that in the approximation considered each level of the molecule is $(2J + 1)$-fold degenerate, interest is presented only by the probability of transition from state J_a to state J_b

$$P_{J_b,J_a}=\sum_{K_b=-J_b}^{+J_b}\sum_{K_a=-J_a}^{+J_a}(2J_a+1)^{-1}|M_{J_b,K_b;J_a,K_a}|^2$$
$$=(2J_b+1)\left(\frac{\pi}{2a_0}\right)\sum_{l=|J_b-J_a|}^{J_a+J_b}(2l+1)J_{l+1/2}^2(a_0)\begin{pmatrix}J_a & J_b & l\\ 0 & 0 & 0\end{pmatrix}^2. \tag{25}$$

From the properties of the 3j symbols it is evident that the probabilities of the direct and inverse transitions are related by the expression

$$P_{J_a,J_b}=[(2J_a+1)/(2J_b+1)]P_{J_b,J_a}. \tag{26}$$

Averaging over the γ-ray emission angles ξ and η in this case, as a consequence of the spherical symmetry, does not lead to new results, $\bar{P}_{J_b,J_a} = P_{J_b,J_a}$.

Expressions (25) and (26) solve the problem of the probabilities of rotational-nuclear transitions for a diatomic molecule in the rigid-rotator approximation. In the special case $J_a = 0$, $J_b = J$ we have

$$\bar{P}_{J,0}=\frac{\pi}{2a_0}(2J+1)J_{J+1/2}(a_0), \tag{27}$$

and in the case $J_a = J$, $J_b = 0$ we have

$$\bar{P}_{0,J}=\frac{\pi}{2a_0}J^2_{J+1/2}(a_0), \tag{28}$$

which is identical to the results of Ref. 7. In Fig. 1 we have given the probabilities of rotational-nuclear transitions from the state $J_a = 0$ to the state $J_b = J$ for $a_0 = 1$ and $a_0 = 10$.

The energy of the γ satellite corresponding to transition of the molecule from rotational state J_a to state J_b in the rigid-rotator approximation according to Eq. (6) is

$$E_\gamma=E_\gamma^{(0)}+\hbar \mathbf{k}_\gamma \mathbf{v}_0 \pm R_{re} \pm B[J_b(J_b+1)-J_a(J_a+1)], \tag{29}$$

where $B = \hbar^2/2m(R^0)^2$ is the rotational constant of the molecule.

6. VIBRATIONAL-ROTATIONAL-NUCLEAR TRANSITIONS

It is well known that the translational degrees of freedom of a molecule on emission or absorption of a γ ray by a nucleus in the molecule take on an energy equal to the recoil energy R_{re}. Let us determine the amount of energy required by the vibrational and rotational degrees of freedom of the molecule. Neglecting rotation, for $v_a = 0$, $\vartheta = 0$ we obtain from Eq. (18) (setting $v_b = v$)

$$P_{v,0}=\frac{z_0^v}{v!}e^{-z_0}. \tag{30}$$

For $z_0 \gg 1$ only $v \approx z_0$ is important in the distribution (30), and since $z_0 = (R_{re}/\hbar\omega)(m_2/m_1)$, the energy which goes into excitation of vibrations is $\epsilon_{vib} \approx v\hbar\omega \approx z_0\hbar\omega = R_{re}(m_2/m_1)$. If we neglect vibrations, then for $J_a = 0$, $J_b = J$, we obtain the distribution (27), in which for $a_0 \gg 1$ only $J \approx a_0$ is important, since $a_0^2 = (R_{re}/B)(m_2/m_1)$, and then an energy $\epsilon_{rot} \approx BJ^2 \approx Ba_0^2 = R_{re}m_2/m_1$ goes into excitation of rotations. Thus, generally speaking, the vibrational and rotational degrees of freedom of a diatomic molecule take on identical energies, which can be either greater than (for $m_2/m_1 > 1$) or less than (for $m_2/m_1 < 1$) the recoil energy.

The energy discussion which we have carried out clearly indicates the need of simultaneously taking into account excitation of vibrations and rotations of a molecule in emission or absorption of a γ ray by a nucleus in the molecule.

The formulas obtained above permit determination of the probability of vibrational-rotational-nuclear transitions of diatomic molecules for not too high vibrational levels, where the harmonic-oscillator approximation is valid. Taking as wave functions $\Psi(\mathbf{R}_1, \mathbf{R}_2)$ the product of the wave functions (15) and (21) and taking into account expression (16), we obtain from Eq. (14) for the matrix element of a vibrational-rotational-nuclear transition a relation similar to Eq. (24):

$$M^{v_b,v_a}_{J_b,K_b;J_a,K_a}=\sqrt{4\pi}[(2J_a+1)(2J_b+1)]^{1/2}(-1)^{K_b} \times\sum_{l=|J_b-J_a|}^{J_a+J_b} i^l[2l+1]^{1/2}\langle\Psi_{v_b}|\left(\frac{\pi}{2a}\right)^{1/2}J_{l+1/2}(a)|\Psi_{v_a}\rangle \times\begin{pmatrix}J_a & J_b & l\\ 0 & 0 & 0\end{pmatrix}\sum_{m=-l}^{+l}Y_{lm}^*(\xi,\eta)\begin{pmatrix}J_a & J_b & l\\ K_a & -K_b & m\end{pmatrix}, \tag{31}$$

where $a = a_0(1+\epsilon) = (E_\gamma^{(0)}/\hbar c)(m_2/M)R^0(1+Q/\sqrt{m}R^0)$, $\Psi_v(Q)$ is the wave function (15). Using the same procedure as in calculation of the probabilities of rotational-nuclear transitions, we obtain for the probability of a vibrational-rotational-nuclear transition from state v_a, J_a to the state v_b, J_b the following expression:

$$\bar{P}^{v_b,v_a}_{J_b,J_a}=(2J_b+1)\sum_{l=|J_b-J_a|}^{J_a+J_b}(2l+1)|\langle\Psi_{v_b}|\left(\frac{\pi}{2a}\right)^{1/2}J_{l+1/2}(a)|\Psi_{v_a}\rangle|^2\begin{pmatrix}J_a & J_b & l\\ 0 & 0 & 0\end{pmatrix}^2. \tag{32}$$

The probabilities of the direct and inverse transitions in this case are related by expressions which follow directly from Eq. (32):

$$\bar{P}^{v_a,v_b}_{J_b,J_a}=\bar{P}^{v_b,v_a}_{J_b,J_a}, \qquad \bar{P}^{v_b,v_a}_{J_a,J_b}=((2J_a+1)/(2J_b+1))\bar{P}^{v_b,v_a}_{J_b,J_a}. \tag{33}$$

We note that if vibrations of the molecule are neglected, i.e., if we set $a = a_0$, then Eq. (25) follows from Eq. (32). In regard to Eq. (19), it cannot be obtained from Eq. (32), as a consequence of the different assumptions regarding symmetry made in derivation of (19) and (32).

In the important case of small oscillations the calculations can be carried through to the end. The condition of smallness of the oscillations is obviously the condition

$$(\overline{Q^2})^{1/2}/\sqrt{m}R^0 \ll 1, \tag{34}$$

or, since for a vibrational level v we have $\overline{Q}^2 1 = (1+2v)/2\alpha$, this condition can be represented in the form

$$(1+2v)^{1/2}\varepsilon_0 \ll 1, \quad \varepsilon_0=(\hbar/2m\omega(R^0)^2)^{1/2}. \tag{35}$$

For diatomic molecules for typical parameter values

$$m\sim(10\div10^2)\ \text{amu},\ \hbar\omega\sim10^2\div10^3\ \text{cm}^{-1},\ R^0\sim2\ \text{Å}$$

we have the value $\epsilon \sim 10^{-3}-10^{-1}$. Therefore for not too large v the condition (35) is satisfied. We expand the function $a^{-1/2}J_{l+1/2}(a)$, using condition (35), in series in the parameter $\epsilon = Q/\sqrt{m}R^0$ and take into account the recurrence relation relating the Bessel function and its derivatives. As a result we obtain

$$a^{-1/2}J_{l+1/2}(a)=a_0^{-1/2}J_{l+1/2}(a_0)+[la_0^{-1/2}J_{l+1/2}(a_0)-a_0^{1/2}J_{l+3/2}(a_0)]\varepsilon +{}^1/_2[l(l-1)a_0^{-1/2}J_{l+1/2}(a_0)-(2l+1)a_0^{1/2}J_{l+3/2}(a_0)+a_0^{3/2}J_{l+5/2}(a_0)]\varepsilon^2+\ldots \tag{36}$$

Using the integrals from Ref. (12), we shall discuss systematically the various approximations.

In the zero approximation only transitions without change of the vibrational quantum number v turn out to be possible and the corresponding probabilities

$$\bar{P}^{v,v}_{J_b,J_a}=(2J_b+1)\frac{\pi}{2a_0}\sum_{l=|J_b-J_a|}^{J_a+J_b}(2l+1)J^2_{l+1/2}(a_0)\begin{pmatrix}J_a & J_b & l\\ 0 & 0 & 0\end{pmatrix}^2 \tag{37}$$

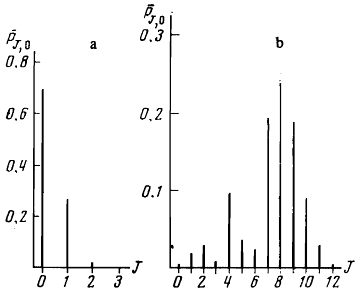

FIG. 1. Probabilities of rotational-nuclear transitions $J_a = 0 \rightarrow J_b = J$ in the rigid-rotator model: a) for $a_0 = 1$, b) for $a_0 = 10$.

in accordance with the remark made above are identical with $\bar{P}_{J_b, J_a}$.

Inclusion of the term in Eq. (36) in ϵ does not change $\bar{P}^{v,v}_{J_b, J_a}$, but in this case transitions with change by unity of the vibrational quantum number also become possible, i.e., transitions for which $v_b - v_a = \pm 1$; their probability is

$$\bar{P}^{v_b, v_a}_{J_b, J_a} = (2J_b+1)\varepsilon_0 \frac{\pi}{2a_0} \mu^1_{v_a} \sum_{l=|J_b-J_a|}^{J_a+J_b} (2l+1) \times (lJ_{l+1/2}(a_0) - a_0 J_{l+3/2}(a_0))^2 \begin{pmatrix} J_a & J_b & l \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{38}$$

where $\mu^1_{v_a} = v_a + 1$ if $v_b - v_a = +1$ and $\mu^1_{v_a} = v_a$ if $v_b - v_a = -1$.

On inclusion of the term in Eq. (36) quadratic in ϵ, the expression for $\bar{P}^{v,v}_{J_b, J_a}$ changes:

$$\bar{P}^{v,v}_{J_b, J_a} = (2J_b+1)\frac{\pi}{2a_0} \sum_{l=|J_b-J_a|}^{J_a+J_b} (2l+1)\{J_{l+1/2}(a_0) + {}^1/_2(1+2v)\varepsilon_0[l(l-1)J_{l+1/2}(a_0) - (2l+1)a_0 J_{l+3/2}(a_0) + a_0^2 J_{l+5/2}(a_0)]\}^2 \begin{pmatrix} J_a & J_b & l \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{39}$$

and expression (38) remains in force. In addition, transitions with change of the vibrational quantum number by two become possible: $v_b - v_a = \pm 2$; their probability is

$$\bar{P}^{v_b, v_a}_{J_b, J_a} = (2J_b+1)\varepsilon_0^2 \frac{\pi}{8a_0} \mu^2_{v_a} \sum_{l=|J_b-J_a|}^{J_a+J_b} (2l+1)[l(l-1)J_{l+1/2}(a_0) - (2l+1)a_0 J_{l+3/2}(a_0) + a_0^2 J_{l+5/2}(a_0)]^2 \begin{pmatrix} J_a & J_b & l \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{40}$$

where $\mu^2_{v_a} = (v_a + 2)(v_a + 1)$ for transitions with $v_b - v_a = +2$ and $\mu^2_{v_a} = v_a(v_a - 1)$ for transitions with $v_b - v_a = -2$.

Obviously, systematic inclusion of each succeeding term of the expansion (36) will lead both to improvement of the previously calculated $\bar{P}^{v_b, v_a}_{J_b, J_a}$, and also to appearance of new transitions whose probability will fall off in accordance with the condition $(1 + 2v)^{1/2}\epsilon_0 \ll 1$.

From Eq. (36) and also from (37)–(40) it can be understood that for diatomic molecules the probability of a vibrational transition is proportional to $\epsilon_0^{v_b - v_a}$, i.e., is determined by the ratio of the amplitude of oscillations to the equilibrium internuclear distance and depends weakly on the γ-ray energy (through its dependence on a_0). A similar result can be proved also for polyatomic molecules with a γ-active nucleus outside the center of symmetry of the molecule, and this differs sharply from the case of symmetric polyatomic molecules with a γ-active nucleus at the center of symmetry, for which the probability of change of the vibrational state is determined by the ratio of the amplitude of vibrations to the γ-ray wavelength.[2]

In contrast to vibrational-nuclear transitions, where the parameter z_0 determining the transition probability varies over a wide range, for the case of vibrational-rotational-nuclear transitions (and also rotational-nuclear transitions) a certain simplification can be achieved in the formulas by replacement of the Bessel functions by their asymptotic expressions, since the quantity a_0 is usually significantly greater than unity. For $a_0 \gg 1$, $a_0 \gg J_a + J_b$ we shall make in Eq. (32) the substitution

$$\left(\frac{\pi}{2a}\right)^{1/2} J_{l+1/2}(a) \approx \frac{1}{a}\sin\left(a - \frac{l\pi}{2}\right), \tag{41}$$

and since $a = a_0(1 + \epsilon)$, we then have

$$\frac{1}{a}\sin\left(a - \frac{l\pi}{2}\right) \approx \frac{1}{a_0}\sin\left(a_0 - \frac{l\pi}{2}\right)\cos a_0\varepsilon + \frac{1}{a_0}\cos\left(a_0 - \frac{l\pi}{2}\right)\sin a_0\varepsilon; \tag{42}$$

here in the denominator we set $a = a_0$ and, in accordance with Eq. (35), neglect small changes in $1/a$ in comparison with significant changes in $\cos a_0\epsilon$ and $\sin a_0\epsilon$. Expression (42) is easily integrated and we finally obtain

$$\bar{P}^{v_b, v_a}_{J_b, J_a} = (2J_b+1)\frac{v_a!}{v_b!} z_0^{v_b - v_a} e^{-z_0}[L_{v_a}^{v_b - v_a}(z_0)]^2 \sum_{l=|J_b-J_a|}^{J_a+J_b} (2l+1) \begin{pmatrix} J_a & J_b & l \\ 0 & 0 & 0 \end{pmatrix}^2 \times \frac{1}{a_0^2} \begin{Bmatrix} \sin^2(a_0 - l\pi/2) \\ \cos^2(a_0 - l\pi/2) \end{Bmatrix}, \tag{43}$$

where the sine and cosine refer respectively to the transitions $v_b - v_a = 2n$ and $v_b - v_a = 2n + 1$, $n = 0, 1, 2, \ldots$; $z_0 = (\epsilon_0 a_0)^2$ is the same quantity as in Eq. (17).

The energies of the γ satellites corresponding to transitions of a diatomic molecule from a state v_a, J_a to a state v_b, J_b in accordance with condition (6) are equal to

$$E_\gamma = E_\gamma^{(0)} + \hbar k_\gamma v_0 \pm R_{re} \pm \hbar\omega(v_b - v_a) + B[J_b(J_b+1) - J_a(J_a+1)]. \tag{44}$$

7. POSSIBLE EXPERIMENTS

Change of the internal state of a molecule on emission of a γ ray by a nucleus in the molecule can be experimentally observed by means of the fluorescence of molecules excited by the recoil. This experimental possibility was pointed out previously in the case of a monatomic gas in Refs. 3 and 4. It must be noted that the use of molecules can present greater interest, since in this case it is possible to observe fluorescence not only from excited electronic states, but also from vibrational-rotational levels of the electronic ground state. This experimental arrangement naturally suggests use of a molecular gas with nuclei in isomeric states.

The structure of the γ spectrum of a nucleus in a molecule, due to change in the internal state of the molecule, can be observed by means of the change in resonance absorption of γ rays by the molecular gas on change of the distribution of molecules in electronic-vibrational-rotational levels. Detection of the change of the cross section for resonance absorption can be accomplished both by counting the number of resonance-scattered γ rays and by the change in the current of internal conversion electrons.[13] In the case where isomeric states of nuclei are utilized, the inverse experimental arrangement is possible, in which the state of the molecular gas radiator changes but one detects a change in the resonance absorption of γ rays by a target containing the same nucleus as the source. In any case the most appropriate method of changing the state of the molecules in the gas is the action on the gas of molecules by coherent laser radiation,[2] which selectively changes the populations of the individual electronic-vibrational-rotational levels of the molecule. It is particularly attractive to use in such experiments diatomic molecules, in which the simple structure of the γ spectra permits us to count on comparing experiment with theory.

As an example of the use of the formulas obtained above, we have shown in Fig. 2 the spectra of emission

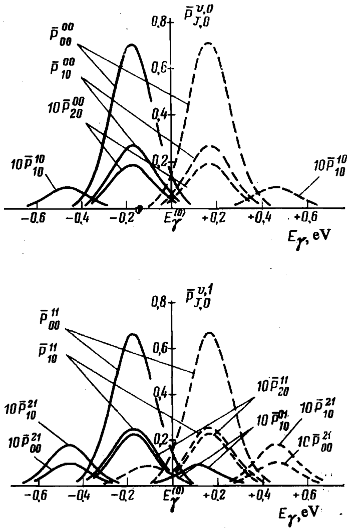

FIG. 2. Spectrum of emission (solid curve) and absorption of the nucleus ^{127}I ($E_\gamma^{(0)} = 203$ keV) bound in the molecule H^{127}I. The initial state of the molecule is as follows: above, $v_a = 0$, $J_a = 0$; below, $v_a = 1$, $J_a = 0$.

and absorption of γ rays of the ^{127}I nucleus with energy $E_\gamma^{(0)} = 230$ keV[10] bound in the molecule H^{127}I which is in its electronic ground state $X^1\Sigma$ (molecular parameters $R^0 = 1.61$ Å, $\nu_e = 2309$ cm^{-1}, $B_e = 6.55$ cm^{-1}), for vibrational-rotational transitions from the state $v_a = 0$, $J_a = 0$ and from the state $v_a = 1$, $J_a = 0$. For this molecule the recoil energy is $R_{re} = 0.172$ eV and the parameters which determine the excitation of rotations and vibrations of the molecule as the result of recoil are respectively $a_0 = 1.30$ and $\epsilon_0 = 5.29 \times 10^{-2}$. The widths of the γ lines correspond to a temperature T = 300 K.

On action of laser radiation on a molecular gas absorber (or radiator) of γ rays, the variation in the cross section for resonance absorption of γ rays by nuclei of molecules of the gas (or correspondingly by nuclei of the target) amounts to the following value[13]:

$$\frac{\Delta\sigma_\gamma}{\sigma_\gamma} = \sum_a \xi^{(2)}_{v_a, J_a} \sum_b \bar{P}^{v_b, v_a}_{J_b, J_a} \exp\left[-\left(\frac{\delta E_{ba}}{\Delta E_D}\right)^2\right] \times \left\{\sum_a \xi^{(1)}_{v_a, J_a} \sum_b \bar{P}^{v_b, v_a}_{J_b, J_a} \exp\left[-\left(\frac{\delta E_{ba}}{\Delta E_D}\right)^2\right]\right\}^{-1} - 1, \tag{45}$$

where $\xi^{(1)}_{v_a, J_a}$, $\xi^{(2)}_{v_a, J_a}$ are the relative populations of the vibrational-rotational levels (v_a, J_a) without laser radiation and in the presence of laser radiation; $\delta E_{ba} = 2R_{re} + \hbar\omega(v_b - v_a) + B[J_b(J_b + 1) - J_a(J_a + 1)]$ is the distance between the absorption and emission lines corresponding to transition of the molecule from the state v_a, J_a to the state v_b, J_b; $\Delta E_D = [(\Delta E_{De})^2 + (\Delta E_{Da})^2]^{1/2}$, where ΔE_{De} and ΔE_{Da} are the Doppler widths of the emission and absorption lines. For the molecule H^{127}I considered by us for T = 300 K we have $\Delta E_D \approx 0.19$ eV and, for example, for saturation of one vibrational-rotational line R(0) of the band 1—0 by radiation of a parametric generator, a change in the relative level populations

$$(\xi^{(1)}_{0,0} \approx 3.13 \cdot 10^{-2}, \; \xi^{(1)}_{1,1} \approx 0)^{[14]}$$
$$\rightarrow (\xi^{(2)}_{0,0} = {}^1/_2 \xi^{(1)}_{0,0} \approx 1.56 \cdot 10^{-2}, \; \xi^{(2)}_{1,1} = \xi^{(2)}_{0,0} \approx 1.56 \cdot 10^{-2})$$

corresponds to a change in the resonance absorption cross section $\Delta\sigma_\gamma/\sigma_\gamma \approx 1\%$.

However, if we achieve saturation of all vibrational-rotational lines of the transition ($v_a = 0 \rightarrow v_b = 1$), i.e., if we excite the vibrational level v = 1 under conditions of rotational relaxation, then it is easy to obtain a variation in the resonance absorption cross section $\Delta\sigma_\gamma/\sigma_\gamma \approx 20\%$.

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