NEW RESONANCES IN AN H_2O MOLECULE

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The dependence of resonance parameters of an H_2O *molecule on the vibrational quantum number* V_2*, associated with the deformation vibration of high amplitude, is numerically studied. A significant change in the inverse inertia tensor* μ_{zz} *due to this vibration and its anharmonicity gives rise to the new types of resonances for which the ordinary conditions of proximity of the frequencies* $\omega_1 \approx \omega_3 \approx 2\omega_2$ *are violated.*

An H_2O molecule belongs to the class of nonrigid molecules. Among the problems, which arise as a result of nonrigidity in processing of the vibrational–rotational spectrum of H_2O, let us note the following: first, a number of the centrifugal constants (CC) of the effective rotational Hamiltonian $H_{\rm rot}$ employed in processing depends anomalously strongly on the quantum number V_2 associated with the deformation (bending) vibration; second, the exponential representation of $H_{\rm rot}$ in terms of the operator of the angular momentum J_z^2 diverges (the z axis is the axis of linearization of the molecule). A theoretical explanation of the anomalously strong dependence of the CC on V_2 was given in Refs. 1–3. The second problem was discussed in Refs. 4–6 and in the literature cited there. The polyads of the resonating vibrational states in an H_2O molecule are formed according to the rule $2V_1 + 2V_3 + V_2 = p = 0, 1, 2, \ldots$, which follows from the condition

$$\omega_1 \approx \omega_3 \approx 2\omega_2 \, . \qquad (1)$$

The resonance interaction between the levels of different polyads was noted in Refs. 7–8, while specific processing of the first decade of H_2O ($p = 6$) was performed in Ref. 9 with an account of the interaction with the vibrational state (070), which formally, from the viewpoint of condition (1), does not belong to this decade.

The authors of Ref. 9 called this resonance HEL–resonance and explained it by a strong centrifugal distortion associated with the excitation of the quantum number V_2.

In this paper, we present the calculated results of the vibrational dependence (on V_2) of different resonance parameters (the Fermi, the Coriolis, and other parameters) of an H_2O molecule and show an existence of different resonances, for which condition (1) is violated and which are primarily caused by an anharmonicity of the potential function of the molecule as well as by the strong dependence of the inverse inertia tensor μ_{zz} on the coordinate of the bending vibration ρ.

THE MODEL OF THE FIELD OF FORCE

The calculations performed in the paper were based on the model of the nonrigid molecule.[10] The technique for calculating the spectroscopic parameters of this model was discussed in Refs. 1 and 3 (for a model of the semirigid molecule the formulas for the resonance parameters can be found in Refs. 11–13). In numerical calculations we employed the anharmonic wave functions $\psi_n(\rho)$ $(n \} V_2)$ obtained by numerical integration of Schroedinger's equation[10,14]:

$$H_0^b\psi_n(\rho) = \left\{ - B_\rho(\rho)\frac{\partial^2}{\partial\rho^2} - \left[\frac{\partial}{\partial\rho} B_\rho(\rho)\right]\frac{\partial}{\partial\rho} + \right.$$

$$\left. + U_0(\rho) + V_0(\rho)\right\}\Psi_n(\rho) = E_n\Psi_n(\rho) \, , \qquad (2)$$

with the prescribed potential function $V_0(\rho)$. The Hamiltonian H_0^b (together with the Hamiltonian $H_0^{Sm\cdot V}$, which describes the harmonic vibrations of low amplitude) is a zero approximation to the Hamiltonian $H = H_0 + W$ when the latter is transformed into the effective Hamiltonian for the polyad of resonating vibrational states. H_0 and the perturbation W are derived from H by expanding the inverse inertia tensor

$$\frac{1}{2}\,\mu_{\rm ab}(\rho,\, q_i) = B_\alpha(\rho)\delta_{\alpha\beta} + \sum_{\rm i} B_i^{\alpha\beta}(\rho)\, q_i +$$

$$+ \sum_{ij} B_{ij}^{\alpha\beta}(\rho)\, q_i\, q_j + \ldots = \{\mu_0\} + \{\mu_1\} + \{\mu_2\} + \ldots \, , \qquad (3)$$

where

$$B_{ij}^{\alpha\beta} = 3/8 \sum_\gamma \left(B_i^{\alpha\gamma} B_j^{\beta\gamma} + B_i^{\beta\gamma} B_j^{\alpha\gamma}\right)/B_\gamma \, ,$$

$i, j = 1, 3$; $\alpha, \beta, \gamma = x, y, z, \rho$, and the potential function

$$V(\rho,\, q_i) = V_0(\rho) + \sum_i K_i(\rho)q_i + \sum_{i,j} K_{ij}(\rho)\, q_i\, q_j +$$

$$+ \sum_{ijl} K_{ijl}(\rho)\, q_i\, q_j\, q_l + \ldots = \{V_0\} + \{V_1\} + \{V_2\} + \{V_3\} + \ldots \qquad (4)$$

into series in terms of the coordinates q_i, which describe the vibrations of low amplitude. For the function $V_0(\rho)$, we have chosen two approximations

$$V_0(\rho) = f_{\alpha\alpha}\, \rho^2 + H\left(1 + f_{\alpha\alpha}\, \rho_e^2/H\right)^2/\left(1 + H\rho^2/f_{\alpha\alpha}\, \rho_e^4\right) \qquad (5)$$

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and

$$V_0(\rho) = f_{\alpha\alpha}\,\rho^2 + f_{\alpha\alpha\alpha}\,\rho^3 + f_{\alpha\alpha\alpha\alpha}\,\rho^4 \,. \qquad (6)$$

The vibrational energy levels with these potentials calculated from Eq. (2) are given in Table I.

TABLE I. The frequencies of the vibrational bands of H_2O *calculated from Eq. (2) and measured experimentally in Refs. 10 and 15* (cm^{-1})*.

Band	Experiment	(5)	(6)	Band	(5)	(6)
ν_2	1594.8	1594.8	1593.7	5 ν_2	7526.6	7536.6
2 ν_2	3151.5	3153.1	3151.3	6 ν_2	8828.4	8859.6
3 ν_2	4666.3	4668.4	4667.4	7 ν_2	10032.4	10124.4
4 ν_2	6134.0	6131.4	6134.6	–	–	–

*The parameters $H = 10960.978\ cm^{-1}$, $F_{\alpha\alpha} = 12857.902\ cm^{-1}$, and $\rho_e = 1.82083$ rad were used for calculation of the potential $V_0(\rho)$ from Eq. (5). The parameters $F_{\alpha\alpha} = 16855.74\ cm^{-1}$, $F_{\alpha\alpha\alpha} = -7522.05\ cm^{-1}$, and $F_{\alpha\alpha\alpha\alpha} = -273.85\ cm^{-1}$ were used for calculation of the potential $V_0(\rho)$ from Eq. (6).

For the functions $F_j(\rho)$, which determine the function

$$K_1(\rho) = (2\pi c)^{-1}(hc\omega_1(\rho))^{-1/2}\sum_j F_j(\rho)\, L_j^i(\rho) \qquad (7)$$

L_j^i (r) is the linear coefficient of conversion of the natural coordinates to the normal, two approximations also wmployed, one of them was given in Refs. 14 and 16, while the second approximation

$$F_j(\rho)/hc = \sum_{i=1}^{4} f_j^{\,i}(\cos\rho_e - \cos\rho)^i \qquad (8)$$

was presented in Ref. 17. The functions $K_{ij}(\rho)$, $K_{ijl}(\rho)$, ... were calculated based on a scheme described in Refs. 14 and 16. The shape of the functions $B_a(\rho)$, $B_i^{ab}(r)$, ... from the kinetic part of the Hamiltonian can be found in Refs. 1 and 3. Let us now consider the dependence of the specific resonance parameters on the quantum number $n \equiv V_2$ employing for them the ordinary terminology.

THE CORIOLIS RESONANCE OF THE FIRST ORDER

The Coriolis resonance of the first order arises as a consequence of the condition $\omega_1 \approx \omega_3$ and for each value of the quantum number $n \equiv V_2$ is described by the operator

$$F_{13}(n) = \{F_{13}^{x}(n)\,(iJ_x) + F_{13}^{yz}(n)(J_y J_z + J_z J_y) + \ldots\} \times$$

$$\times\, |n\rangle\,\langle n| a_1^{+} a_3 + \text{h. c.}\,, \qquad (9)$$

in which h. c. denotes the Hermitian conjugate,

$$F_{13}^{x}(n) = \langle n|B_x\,\zeta_{13}^{x}|n\rangle c(\omega_1 + \omega_3)(\omega_1\omega_3)^{-1/2}\,; \qquad (10)$$

$$F_{13}^{yz}(n) = B_{13}^{yz}(n) - \frac{3}{2}K_{133}(n)\,B_3^{yz}(n)\left\{\frac{\omega_3}{\omega_1(2\omega_3 - \omega_1)} + \frac{1}{\omega_3}\right\}, \qquad (10a)$$

and a_i^{+}, a_j $(i, j = 1, 3)$ are the creation and annihilation operators of the vibrational quanta,[5] which correspond to the vibrations of low amplitude. In formula (10), the following notations were used: $f(n) = f(nn)$, $f(nm) = \langle n|f(\rho)|m\rangle$, and $\omega_i = K_{ii}(\rho_e)$. Taking the values of the functions $B_x(\rho)$, , ... at the point ρ_e out from inside the integrals, we obtain the same relations for these resonance parameter as for the model of a semirigid molecule independent of V_2 (see Refs. 11–13). The calculations of $F_{13}^{x}(n)$ and $F_{13}^{yz}(n)$ performed with different fields of force showed that these parameters can strongly depend on V_2. The typical calculated behavior of these parameters is shown in Fig. 1 (the contributions of the reduction of the effective Hamiltonian[19] to the resonance parameters are ignored in this paper). The asterisk denote the values of the parameters obtained by processing of the experimental data (the change of a sign of the parameters of the operators for the Coriolis resonances has no effect on the reconstruction of the parameters).[20, 21]

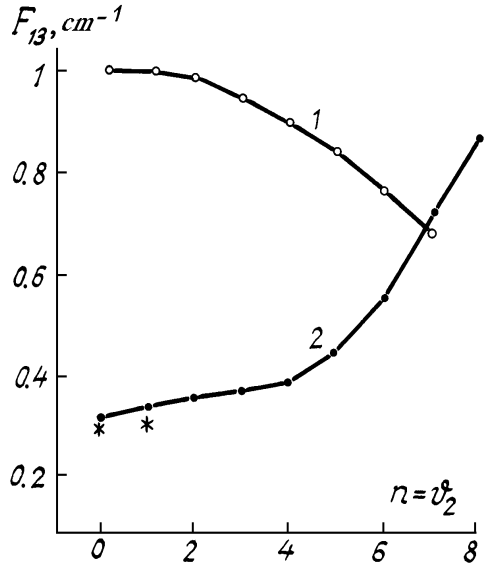

FIG. 1. The calculated dependence of the parameters $F_{13}^{x}(n)$ *(curve 1) and* $F_{13}^{yz}(n)$ *(curve 2) of the Coriolis resonance of the first order.* $V_0(\rho)$ *calculated from Eq. (5) and the field of force taken from Ref. 18 were used.*

THE CORIOLIS RESONANCES OF THE SECOND ORDER

In the model of a semirigid molecule the Coriolis resonances of the second order arise as a consequence of the condition $\omega_3 \approx 2\omega_2$. In the model of a nonrigid molecule they are described by the operator

$$F_3(n, m) = \{F_3^{x}(n, m)\,(iJ_x) + F_3^{yz}(n, m)(J_y J_z + J_z J_y)\ \ldots\} \times$$

$$\times\, |n\rangle\,\langle m| a_3^{+} + \text{h. c.}\,, \qquad (11)$$

which makes it possible to describe all feasible resonances, which arise as a consequence of the condition $\omega_3 + \Omega_{n0} \approx \Omega_{m0}$ $(\Omega_{mn} = E_m - E_n)$. It is obvious that the condition $\omega_3 \approx 2\omega_2$ is a particular case of this condition for $m = n + 2$. The values of the first resonance parameter

$$F_3^x(n,\ m) = -\sqrt{2}\left\{\ T_3^x(nm) + \frac{1}{2}\sum_s{}^{*} K_{33}(ns)\ T_3^x(sm) \times\right.$$

$$\left.\times\left[(\Omega_{sm} + \omega_3)^{-1} + \Omega_{sn}^{-1}\right]\right\} \qquad (12)$$

were calculated from formula (11), where $T_3^x(nm) = \langle\Psi_n(\rho)|B_3^x(\rho)|\partial\Psi_m(\rho)/\partial\rho\rangle$, while the asterisk adjacent to Σ denotes that the terms with resonance denominators are eliminated from the sum. The calculated ehavior of the parameters $F_3^x(n,\ n+2)$ and $F_3^x(n,\ n+3)$ is shown in Fig. 2.

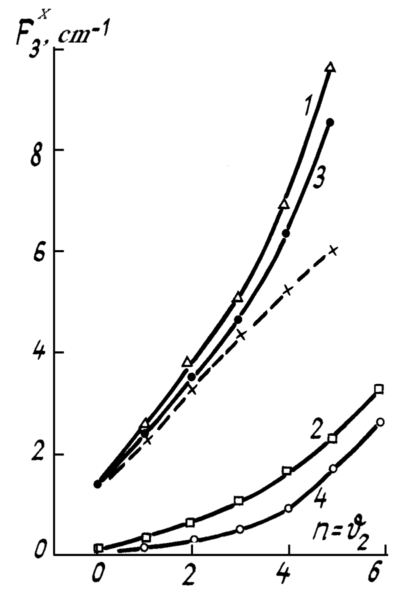

FIG. 2. The calculated dependence of the parameters $F_3^x(n,\ n+2)$ (curve 1) and $F_3^x(n,\ n+3)$ (curve 2) of the Coriolis resonance of the second order. The field of force was used according to Ref. 18 and $V_0(\rho)$ was calculated from Eq. (5). The dashed line indicates the results of calculation based on the model of semirigid molecule: $F_3^x(V_2,\ V_2+2) = \text{const}\cdot\sqrt{(V_2+1)(V_2+2)}$. Curves 3 and 4 shows the results of calculations with the field of forces according to Ref. 17.

The figure shows that for certain values of n and p $|F_3^x(n,\ n+2)| \sim |F_3^x(p,\ p+3)|$ and, moreover, for definite n, $\kappa_c(n,\ n+2) \sim \kappa_c(n,\ n+3)$; $\kappa_c(n,\ m = {}^{x})(n,\ m)|/[(\omega_3 + \Omega_{n0}) - \Omega_{m0}] = {}= {}^{x})(n,\ m)|/(\omega_3 + \Omega_{mn})$. This means that two vibrational states ($kn1$) and ($km0$) ($m = n+2$, $n+3$, k is the arbitrary parameter) must be joined into a single polyad. In our calculations such a situation realizes for $n = 2$ and, in particular, the state (021) must be considered simultaneously with the states (040) and (050). It is evident from formula (12) that such resonances are described by the contributions of the kinetic (T_3^x) and potential parts of the Hamiltonian.

THE DARLING–DENNISON RESONANCE

The Coriolis resonances of the second order arises as a consequence of the condition $2\omega_1 \approx 2\omega_3$ and is described by the operator

$$F_{13}^D(n) = F_{13}^0(n)\ a_1^+a_1^+a_3a_3 + \text{h. c.}\ , \qquad (13)$$

in which

$$F_{13}^{(0)}(n) = \frac{1}{2}\left\{3K_{1133}(n) - \frac{3K_{133}^2(n)}{\mathrm{w}_1} +\right.$$

$$\left.+\frac{3}{2}\frac{K_{111}(n)\kappa_{133}(n)}{\omega_1} - \frac{1}{8}\sum_s{}^{*}\frac{K_{11}(ns)K_{33}(sn)}{\Omega_{sn}}\right\}. \qquad (14)$$

In the calculations carried out as well as in the model of a semirigid molecule, $F_{13}^{(0)}$ is virtually independent of n.

THE FERMI RESONANCE

In the model of a semirigid molecule, the Fermi resonance arises as a consequence of the condition $\omega_1 \approx 2\omega_2$. In general, it is described by the operator

$$F_1(n,\ m) = \left\{F_1^{(0)}(n,\ m) + \sum_{\alpha=xyz} F_{1\alpha}(n,\ m)\ J_\alpha^2 + \ldots\right\}\times$$

$$\times\ |n\rangle\langle m\ |a_1^+ + \text{h. c.}\ . \qquad (15)$$

The case $\omega_1 \approx 2\omega_2$ is realized when $m = n + 2$. In formula (15)

$$F_1^{(0)}(n,\ m) = \frac{1}{\sqrt{2}}\tilde{K}_1(nm) =$$

$$= \frac{1}{\sqrt{2}}\left\{K_1(nm) - \langle\Psi_n|B_1^{qq}(\rho)|\frac{\partial^2\Psi_m}{\partial\rho^2}\rangle\right\}. \qquad (16)$$

The relation for $F_{1\alpha}$ can be symbolically written down in the form

$$\{F_{1\alpha}\} = \{\mu_1\} + \{\mu_0 \times V_1\} + \{\mu_1 \times V_2\} + \{\mu_2 \times V_1\} +$$

$$+ \{T(\text{cor}) \times \mu_1^\rho\} + \{\mu_1^\rho \times \mu_1^\rho\} +$$

$$+ \{V_1 \times \mu_1 \times V_3\} + \{V_1 \times V_1 \times \mu_1\} + \{V_2 \times \mu_0 \times V_1\} +$$

$$+ \{T(\text{cor}) \times V_2 \times \mu_1^\rho\} + \{\mu_1^\rho \times \mu_1^\rho\} \times \{V_1 + V_3\} +$$

$$+ \{T(\text{cor}) \times T(\text{cor}) \times V_1\}\ , \qquad (17)$$

in which μ_i^ρ means that one of the indices α and β in $\{\mu_i\}$ assumes the value ρ, while $T(\text{cor})$ is the term of W, which includes the Coriolis constant.[11] Of all parameters $F_{1\alpha}(\alpha = x,\ y,\ z)$, F_{1z} is the largest in magnitude and most sensitive to the variations of the quantum number V_2. The numerical calculations showed that in order to determine F_{1z} it is necessary to retain only two terms in formula (17). Then,

$$F_{1z}(n,\ m) = F_{1z}^{(nm)}(\text{cent}) + F_{1z}^{(nm)}(\tilde{a})\ , \qquad (18)$$

$$F_{1z}^{(nm)}(\text{cent}) = \frac{1}{\sqrt{2}}\, B_1^{zz}(nm)\ ;$$

where

$$F_{1z}^{(nm)}(\tilde{a}) = \frac{1}{2\sqrt{2}} \sum_s{}^{*}\ \{B_z(ns)\tilde{K}_1(sm) \times$$

$$\times \left[(\Omega_{ns} + \omega_1)^{-1} - \Omega_{sm}^{-1}\right]\ . \qquad (19)$$

The calculated behavior of the parameters $F_1^{(0)}(n,\ m)$ and $F_{1k}(n,\ m) = F_{1z}(n,\ m) - \left(F_{1x}(n,\ m) + F_{1y}(n,\ m)\right)/2$ is shown in Figs. 3 and 4.

The estimate of the quantity $\kappa_F(n,\ m) = \left|F_{1k}(n,\ m)\ /(\ \omega_1 - \Omega_{mn}\right)$ shows that a number of states with $\nu_1 + n\nu_2$ and $m\nu_2$ with $m = n + 2$ and $n = 3$ and even with $m = n + 4$ for large n should be joined into a single polyad (in particular, the state (130) should be considered simultaneously with the states (050) and (060), the state (140) ––with (060) and (070), etc.). The values of two contributions calculated from formula (18) to the parameter F_{1z} are given in Table II.

TABLE II. The contributions, calculated from formula (18), to the parameter F_{1z} (nm) *of the Fermi resonance* (cm^{-1}).*

n	m	$F_{1z}(\text{cent})\cdot 10$	$F_{1z}(\tilde{a})\cdot 10$	$F_{1z}\cdot 10$
0	2	−1.9	2.5	0.6
1	3	−4.0	7.0	3.0
1	4	−1.3	7.8	6.5
2	5	−3.0	21.0	18.0

*Formula (15) was used to calculate $V_0(\rho)$ and the field of force was assigned according to Ref. 18.

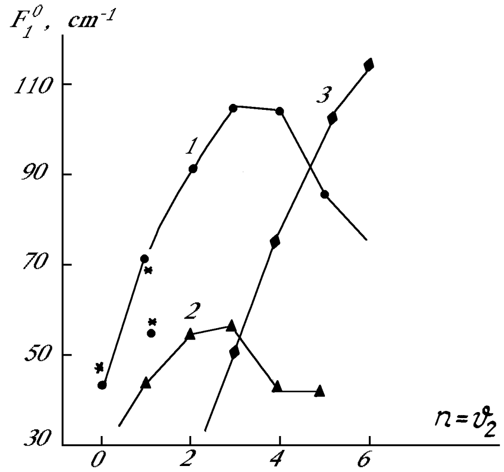

FIG. 3. The calculated values of the parameters $F_1^{(0)}(n,\ n + 2)$: *1) the calculation with the field of force according to Ref. 18; 2) calculation with the field of force according to Ref. 17; 3) parameter* $F_1^{(0)}(n,\ n + 3)$ *with the field of force for the Fermi resonance according to Ref. 18. The asterisks denote the experimental data according to Refs. 20 and 21.*

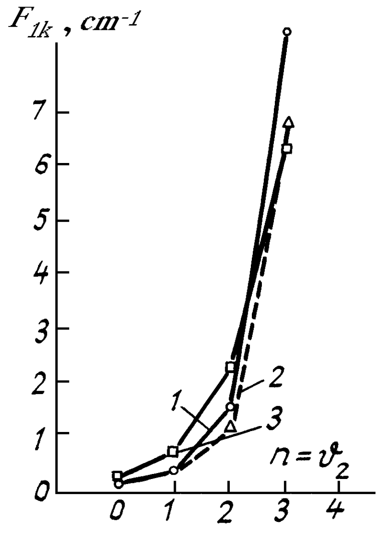

FIG. 4. The calculated dependence of the parameters $F_{1k}(n,\ n + 2)$; *1) calculation with the field of force according to Ref. 18; 2) calculation with the field of the force according to Ref. 17; 3) the* $F_{1k}(n,\ n + 3)$ *with the field of force according to Ref. 18 vs the quantum number* $n = V_2$ *for the Fermi resonance.*

It can be seen from the table that these contributions for small n are approximately identical and have the opposite signs. At large n, the contribution of $F_{1z}(\tilde{a})$ predominates. It is interesting to note the following. If the Hamiltonian $\tilde{\mathrm{H}}_0 = \mathrm{H}_0 + \mathrm{B}_z(\rho)Jn_z^2$ (see Ref. 4) is taken as a zero-order approximation of H_0, F_{1k} will be described by the contribution $F_{1k}(\text{cent})$. In so doing, the calculated values of $F_{1k}(0,\ 2)$ and $F_{1k}(1,\ 3)$ approximately agree with the experimental values of F (see Refs. 17 and 18).

THE FERMI RESONANCE OF THE FORTH ORDER

In the model of a semirigid molecule the Fermi resonance of the forth order arises as a consequence of the condition $2\omega_1 \approx 4\omega_3$. In the model of an nonrigid molecule it is described by the operator

$$F_{11}(n,\ m) = \{F_{11}^{(0)}(n,\ m) + \sum_{\alpha = xyz} F_{11\alpha}(n,\ m)\ J_\alpha^2 + \ldots\} \times$$

$$\times\ |n\rangle\ \langle m| a_1^{+} a_1^{+} + \text{h. c.}\ , \qquad (20)$$

in which

$$F_{11}^{(0)}(n,\ m) = \frac{1}{4}\, K_{11}(n,\ m)\ , \qquad (21)$$

while F_{11a} can be represented by the sum of three terms

$$\{F_{11\alpha}\} = \{\mu_2\} + \{\mu_0 \times V_2\} + \{\mu_1 \times V_1\} =$$

$$= \{F_{11\alpha}(\text{cent})\} + \{F_{11\alpha}(h)\} + \{F_{11\alpha}(\tilde{a})\}\ . \qquad (22)$$

The specific form of these terms is as follows:

$$F_{11\alpha}^{(nm)}(\text{cent}) = 3/8\ B_{11}^{\alpha\alpha}(nm)\ ; \qquad (23)$$

$$F^{(nm)}_{11\alpha}(h) = -1/8\sum_{s}{}^{*}\{B_\alpha(ns)\,K_{11}(sm) +$$

$$+ K_{11}(ns)\,B_\alpha(sm)\}(\Omega^{-1}_{sn} + \Omega^{-1}_{sm})\;; \tag{23a}$$

$$F^{(nm)}_{11\alpha}(\tilde{a}) = -1/4\sum_{s}{}^{*}\{\tilde{K}_1(ns)\,B_1^{\alpha\alpha}(sm) +$$

$$+ B_1^{\alpha\alpha}(ns)\tilde{K}_1(sm)\}\left[(\Omega_{sn} - \omega_1)^{-1} + (\Omega_{sm} + \omega_1)^{-1}\right]. \tag{23b}$$

In Table III, all contributions to the parameter $F_{11z}(n, n + 5)$ for $n = 0, 1, 2$ and, for comparison, to $F_{11z}(1, 7)$ are written down. The behavior of the parameters $F_{11k}(n, m)$ for different n and m follows the behavior of the parameters $F_{1k}(n, m)$ shown in Fig. 4.

TABLE III. Values of contributions of terms of Eq. (22) to the parameter $F_{11z}(nm)$ of the Fermi resonance of the forth order (cm^{-1})*.

n	m	F_{11z}(cent)	$F_{11z}(h)$	$F_{11z}(\tilde{a})$	F_{11z}
0	5	4.7E–4	4.7E–4	–1.5E–2	–1.4E–2
1	6	2.5E–3	4.1E–3	–1.1E–1	–1.0E–1
2	7	1.3E–2	2.9E–2	–8.8E–1	–8.4E–1
1	7	7.8E–3	4.2E–3	7.0E–2	7.6E–2

*The value of $V_0(\rho)$ given by Eq. (6) and the field of force according to Ref. 18 were used.

These results were obtained with the functions $V_0(\rho)$ given by Eq. (6) and $K_1(\rho)$ given by Eq. (7). The estimate $\kappa_{FF}(n, m) = |F_{11}(nm)|/(2\omega_1 - \Omega_{mn})$ shows that the state $2\nu_1 + n\nu_2$ (for arbitrary ν_3) should be joined into a single polyad with the state $m\nu_2$ starting from $n = 1$ and $m = n + 4$, $n + 5$ and in some cases to $m = n + 6$. The new resonance described in Ref. 9 arises in the case under consideration for $n = 2$ and $m = n + 5$. Table III shows that the contributions of the terms $F_{11z}(h)$ and $F_{11z}\tilde{a}$ associated with the anharmonicity of the potential function $V(\rho, q)$ given by formula (4) and with the expansion of μ_{zz} given by Eq. (3), to the parameter $F_{11z}(n, n + 5)$ predominate.

CONCLUSION

The results of calculations showed that the effects of nonrigidity in an H_2O molecule violates the rule of formation of the polyads of resonating vibrational states based on Eq. (1). Thus, n–fold excitation of the quantum number $V_2 (n \geq 1)$ makes it impossible to strictly separate one polyad from another owing to the resonance interaction of the state (V_1, nV_2, V_3) with the state (V_1', mV_2, V_3') when $m \neq n + 2$. The matrix coefficients, which relate these states, just as for the ordinary Fermi and Coriolis resonances, are formed both by the terms of the kinetic part of the Hamiltonian and by the terms of the expansion of the potential function of the molecule. In addition, the values of these matrix coefficients increases sharply with increase of the quantum number V_2.

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REFERENCES

1. V.I. Starikov, B.N. Makhancheev, and Vl.G. Tyuterev, in: *Spectroscopy of Atmospheric Gases* (Nauka, Novosibirsk, 1982), pp. 34–54.
2. V.I. Starikov, B.N. Makhancheev, and Vl.G. Tyuterev, J. Phys. Lett. **45**, L–11–L–15 (1984).
3. V.I. Starikov and Vl.G. Tyuterev, J. Mol. Spectr. **95**, 288–296 (1982).
4. Vl.G. Tyuterev, V.I. Starikov, and V.I. Tolmachev, Dokl. Akad. Nauk SSSR **297**, 345–349 (1987).
5. Yu.S. Makushkin and Vl.G. Tyuterev, *Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy* (Nauka, Novosibirsk, 1984), 214 pp.
6. O.L. Polynsky, J. Mol. Spectr. **112**, 79–87 (1985).
7. J.M. Flaud, C. Camy–Peyret, K.N. Rao, et al., J. Mol. Spectr. **75**, 339 (1979).
8. J.Y. Mandin, J.P. Chevilard, J.M. Flaud, and C. Camy–Peyret, Can. J. Phys. **66**, 997–1011 (1988).
9. A.D. Bykov, O.V. Naumenko, and L.N. Sinitsa, Opt. Atm. **3**, No. 10, 1014 (1990).
10. J.T. Houger, P.R. Bunker, and J.W.G. Johns, J. Mol. Spectr. **34**, 136–172 (1970).
11. V.I. Perevalov and Vl.G. Tyuterev, Opt. Spektrosk. **51**, 640–647 (1981).
12. V.I. Perevalov and Vl.G. Tyuterev, *Centrifugal Distortions in Assymmetric–Top Molecules with Random Resonances*, Institute of Atmospheric Optics, Preprint No. 30, Tomsk, 1979, 65 pp.
13. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulennikov, *Vibrational–Rotational Spectroscopy of Water Vapor* (Nauka, Novosibirsk, 1989), 296 pp.
14. A.R. Hoy and P.R. Bunker, J. Mol. Spectr. **52**, 439–456 (1974).
15. C. Camy–Peyret, J.M. Flaud, and J.P. Maillard, J. Phys. Lett. **41**, L–23–L–26 (1980).
16. P. Jensen and P.R. Bunker, J. Mol. Spectr. **99**, 348–356 (1983).
17. P. Jensen, J. Mol. Spectr. **133**, 438–460 (1989).
18. A.R. Hoy, J.M. Mills, and G. Strey, Mol. Phys. **24**, 1265–1290 (1972).
19. V.I. Perevalov and Vl.G. Tyuterev, Opt. Spektrosk. **52**, 644–650 (1982).
20. J.M. Flaud and C. Camy–Peyret, J. Mol. Spectr. **51**, 142–150 (1974).
21. C. Camy–Peyret and J.M. Flaud, J. Mol. Spectr. **59**, 327–332 (1976).