APPROXIMATION OF *K*–DEPENDENCE OF THE $(HF)_2$ DIMER ROTATIONAL ENERGY

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The dependence of the rotational energy F(K) of the $(HF)_2$ *dimer on the rotational quantum number K is investigated. This investigation is based on the simultaneous analysis of high–amplitude bending vibration and molecular rotation. The analytical representations of the rotational energy F(K) are obtained, which can be used for retrieval of the numerical values of the function F(K) by fitting the experimental data for the hypothetical level J = 0. As compared to the polinomial and fractional–rational representation of dependences of the rotational energy F(K) on the quantum number K, our models provide the better account for the experimental data and posess better extrapolation properties.*

The $(HF)_2$ dimers are classified among as nonrigid molecules with strong vibrational–rotational interaction associated with high–amplitude bending vibrations of a molecule. This class of molecules also incorporates a large number of the H_2X molecules among them, e.g., the H_2O molecule, which in many respects determines radiation absorption in the atmosphere in the visible and infrared. A variety of both fundamental and purely calculational problems of high–resolution spectroscopy in the study of spectra of such molecules arise from nonrigidity effects of centrifugal distortion. The potential function of the $(HF)_2$ molecule related to those atomic motions which retain the molecule flat (the trans–path is considered) has a low barrier relative to an intermediate configuration with the C_{2h}–symmetry (about 330 cm^{-1}, Ref. 1) that allows the molecule to convert from one bending configuration to the other equivalent to it. Such an inversive motion results in the inversion–rotational molecular spectrum whose experimental study was started by Dyke et al.[2] (references to other experimental works can be found in Ref. 3). The group–theoretical analysis of vibrational–rotational motion of the $(HF)_2$ dimer is given in Refs. 2, 4, and 5.

From theoretical point of view nonrigidity of molecule leads to the problem of correct consideration of strong bending–rotational interaction and as a result, to the problem of searching for the dependence of rotational molecular energy on rotational quantum numbers adequately describing the experimental data. It is well known that the high–amplitude bending vibration of triatomic nonrigid molecules H_2X leads to divergence of the polinomial representation of the effective rotational Hamiltonian H_w (see, e.g., Refs. 6 and 7). The subsequences which incorporate powers of the operator J_z^2 (Z is the axis of linearization of the molecule) have the worst convergence of the H_w expansion. In the basis of rotational wave functions $|J, K>$ the operator J_z^2 is diagonal, i.e., $J_z^2|J, K> = K^2|J, K>$. A diagonal part of the Hamiltonian H_w in the standard representation corresponds to the function

$$<J, K|H_W|J, K> = F_N(K) = \sum_{i=0}^{N} C_i K^{2i} \tag{1}$$

with J–dependent constants C_i. One of the evident manifistantions of nonrigidity consists in the fact that the achievement of high accuracy of describing the experimental data requires a large number of adjustable parameters C_i in Eq. (1). These parameters are purely phenomenological and do not allow one to calculate highly excited rotational molecular energies with an acceptable accuracy.

This is manifested especially strongly with the (HF_2) dimers. The relation for the energy of inversion–rotational levels employed for fitting the inversion–rotational transitions can be written in the form[3]

$$E_K^V = \mathrm{D}_V + F^V(K) + \bar{B}\, J(J+1) -$$

$$- D^V_{J,k}[J(J+1)]^2 + H^V_J[J(J+1)]^3 + \ldots$$

$$\pm \left\{\frac{1}{4}(\mathrm{B} - \mathrm{C})^{\mathrm{V}} J(J+1) + d_2^V[J(J+1)]^2 + \ldots\right\}. \tag{2}$$

The constant Δ_V determines the amount of the inversion doubling of vibrational energy levels ($V = 0, 1, 2, \ldots$), the function $F(K)$ determines the dimer rotational energy as a function of the quantum number K, the terms incorporating the constants $\bar{B}$, D, ... together with $F(K)$ describe rotational energy of nonrigid symmetric top, and finally the terms in braces describe the correction for the energy associated with the molecular asymmetry. The function $F(K)$ describing a centrifugal distortion in the symmetric–top molecule approximation has the conventional form

$$F(K) = (A - B)\,\bar{K}^2 - D_K K^4 + H_K K^6 + \ldots\ . \tag{3}$$

Hereafter, the superscript V is omitted for brevity.

Lafferty et al.[3] showed that to ensure an experimental accuracy of retrieval of the inversion–rotational transition frequences entering in the function $F(K)$ by fitting it is necessary to employ as many number of the adjustable parameters A, D_k, ... as the number of the functions $F(K)$ known from the experiment. This means that the functional representation of Eq. (3) is not consistent with real behavior of the experimental data. By virtue of this fact the experimental data were fitted individually for each K–band (K = 0, 1, and 2) so that in the energy E_K given by Eq. (2) there were not the parameters of the function $F(K)$ which were retrieved by solving the inverse spectroscopic problem, but rather the numerical values of the function *F(K)* for the given K. Series (3) cannot apparently be employed for

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predicting rotational energies (or transition frequencies) with quantum numbers $K > K_{\max}$, where $K_{\max}$ is the maximum value of the quantum number for experimental energy levels (or transition frequencies) used for the determination of the parameters of the function $F(K)$. Figure 1shows the values of the function $F_N(K)$ of the $(HF)_2$ dimer calculated from Eq. (1) with $K > N$ represented for the vibrational state $V = 1$ (the upper inversion component of the ground vibrational state) and $J = 0$. In the functions $F_N(K)$ the value N determines the number of the adjustable parameters obtained by fitting the first N values of the function $F(K)$. The experimental (more exactly, obtained by fitting the experimental data) values of the function $F(K)$ are joined by a solid line.

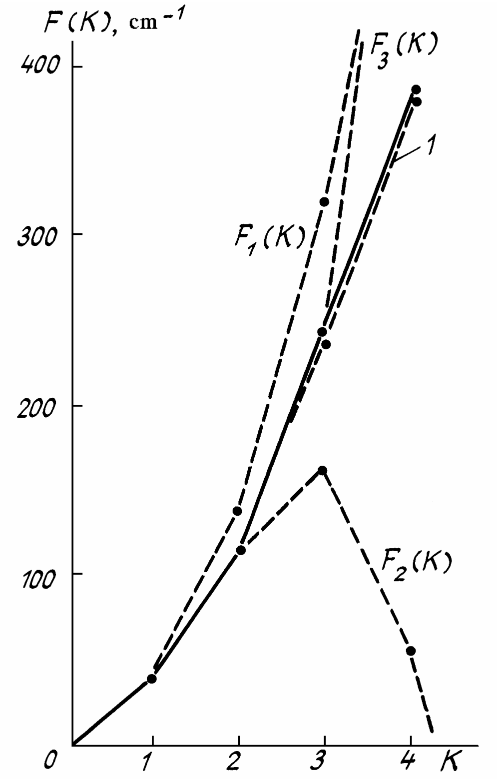

FIG. 1. Experimental (solid line) and calculated (dashed lines) values of the ground–state rotational energy (the component $V = 1$) of the $(HF)_2$ dimer (for the hypothetical level $J = 0$). Dashed lines correspond to the results of calculation with the polynomial representation of $F_N(K)$ incorporating the N adjustable parameters determined by fitting the N experimental data. Curve 1 corresponds to the results of calculation with two–parametric function (11).

In Ref. 3 the Pade representation of the energy E_K was used in addition to conventional representations (2) and (3). Though the number of the adjustable parameters in fitting the experimental data was the same as for the Taylor representation of Eqs. (2) and (3) for E_K, the quality of predicting highly excited energy levels, as was noted in Ref. 3, was substantially improved.

This paper is devoted to approximation of K–dependence of the $(HF)_2$ dimer rotational energy, i.e., search for an optimal analytical representation of the $F(K)$ function whose experimental values (for a hypothetical level $J = 0$) have been given in Refs. 1 and 3.

METHOD OF INVESTIGATION

Method for studying the rotational energy of nonrigid molecule as a function of the quantum number K is based on simultaneous consideration of high–amplitude vibration and rotation in Schrodinger's equation

$$\left\{-\mu\frac{\partial^2}{\partial\rho^2} + V_0(\rho) + \tilde{A}(\rho)\,K^2\right\}\Psi = h(K)\Psi\ , \tag{4}$$

where ρ is the coordinate of high–amplitude bending vibration for $(HF)_2$ determined in Ref. 1, $V_0(\rho)$ is the anharmonic potential function corresponding to a given vibration and assuming a rigorous solution of Eq. (4) for $K = 0$. The function $\tilde{A}(\rho)$ models the behavior of the function $A(\rho)$ as a function of variation in the molecular inertia tensor along the axis of linearity (an explicit form of this function can be calculated using the formulas given in Ref. 1). The method was proposed for the description of the rotational energy of the nonrigid H_2X molecules in Refs. 8–11. Equation (4) represents the model analog of a more complete equation which was solved, e.g., in Refs. 1 and 12 using the numerical methods. Is this case the function $h(K)$ provides a point–by–point values of rotational energy of molecule ($J = 0$) for each K.

Is should be noted that if the function $A(\rho)$ is expanded in a quickly convergent series in terms of the coordinate ρ then such an expansion also results in convergence of polynomial representation of $F(K)$. This is not the case for the $(HF)_2$ dimer. The calculated values of the function $A(\rho)$ are given in Ref. 1. They are successfully approximated by the function (see Table I):

$$\tilde{A}(\rho) = \left\{\tilde{A}(\rho)\right\} + \left\{\Delta\tilde{A}(\rho)\right\} = \left\{a_0 + \frac{a_1}{\rho^2}\right\} + \left\{\frac{a_2}{\rho}\right\} \tag{5}$$

with the parameters a_i ($i = 0, 1, 2$). It can be seen from Eq. (5) that as $\rho \to 0$ (when $\rho = 0$ the molecule is linear and has finite barrier with respect to linearity in the potential $V_0(\rho)$) the function $\tilde{A}(\rho)$ increases without limit, i.e., $\tilde{A}(\rho) \to 8$, so that the contribution of $\tilde{A}(\rho)\,K^2$ associated with the rotation of molecule and variation in the inertia tensor becomes of primary importance in Eq. (4).

TABLE I. The values of the function A(p) (see Ref. 1) and its model representations $\tilde{A}_0(\rho) = a_0 + a_1/\rho^2$ *and* $\tilde{A}(\rho) = A_0(\rho) + a_2/\rho$ (cm⁻¹) *

ρ (°)	$A(\rho)$ Ref. 1	$\tilde{A}_0(\rho)$	$\tilde{A}(\rho)$
0.1	1417673.8	1417673.8	1417672.7
1.0	14319.6	14210.6	14319.2
5.0	604.9	601.3	605.9
10.0	165.2	176.0	166.4
20.0	52.0	69.7	52.8
34.4	26.2	46.2	26.3
50.0	19.2	39.9	18.6
70.0	15.9	37.1	15.0
90.0	14.8	36.0	13.4

* $a_0 = 10.04$ cm⁻¹, $a_1 = 4.313953$ cm⁻¹· rad², and $a_2 = 2.57077272$ cm⁻¹· rad.

The potential function $V_0(\rho)$ of a molecule ($V_{\min}$ in the notation of Ref. 1), *ab initio* values of which are given in Ref. 1, can be fitted by different functions assuming the solution of Eq. (4) for $K = 0$ (see, e.g., Ref. 10). It is convenient to choose this function in the form

$$V_0(\mathrm{r}) = b_0 + b_1/\rho_2 + b_2\,\rho^2\,, \tag{6}$$

which assumes the solution of Eq. (4) (simultaneously with the function $\tilde{A}_0(\rho)$) for $K \neq 0$ and ensures approximately the same quality of retrieval of *ab initio* values of $V_{\min}$ as of the other functions $V_0(\rho)$ from Ref. 10.

MODEL REPRESENTATIONS OF ROTATIONAL ENERGY OF THE $(HF)_2$ DIMER

Substitution of $V_0(\rho)$ given by Eq. (6) and the function $\tilde{A}(\rho)$ from Eq. (5) into Eq. (4) (contribution of $\Delta\tilde{A}(\rho)K^2$ is taken outside it into the perturbation) yields[9,11,13]

$$h(K) = \sqrt{b_2\mu}\left(4n + 2 + \sqrt{1 + 4\,(b_1 + a_1\,K^2)/\mu}\right) + a_0K^2. \tag{7}$$

To determine the molecular rotational energy scaled to the energy with $K = 0$ it is convenient to employ the function

$$G(K) = \tilde{\mu}\left(\sqrt{1 + \alpha_1K^2} - 1\right)\,, \tag{8}$$

where

$$\tilde{\mu} = \frac{1}{4}\,\omega\,\sqrt{1 + 4b_1/\mu}\,,\quad \alpha_1 = \frac{4a_1}{\mu + 4b_1}\,,\ \text{and}\ \omega = 4\sqrt{b_2\mu}\,. \tag{9}$$

In these designations for vibrational state $n = 0$ (it is degenerated and incorporates two components $V = 0$ and $V = 1$) we have

$$h(K) - h(0) = G(K) + a_0K^2\,. \tag{10}$$

Since for $K \gg 1$ the asymptotic is $G^2(K) \sim CK^2$ (hereafter C are arbitrary constants), we can represent the function $F(K)$, using Eq. (10) for consistency, in the form

$$F(K) = G(K) + g_2G^2(K)\,, \tag{11}$$

where g_2 is the adjustable parameter. The calculated behavior of the function $F(K)$ given by Eq. (11) with the two adjustable parameters α_1 and g_2 retrieved from the values of the functions $F(K = 1)$ and $F(K = 2)$ is shown in Fig. 1. The value $\tilde{\mu} \cong \omega/4$ for $\omega = 160\ \mathrm{cm}^{-1}$ (see Ref. 1) was used for the parameter $\tilde{\mu}$.

The function $G(K)$ determined by formula (8) has the form of a generating function being introduced in Refs. 9 and 11 for describing the energies of the rotational levels of the H_2O molecule. The expansion of this function in the Taylor series in terms of α_1K^2 gives polynomial representation (1) which is conventional for $F(K)$. The values of the parameters C_i of this representation are close in values to those obtained from fitting the experimental data. In contrast to the H_2O molecule, in the function $G(K)$ for the $(HF)_2$ dimer the parameter $\alpha_1 \cong 2.6 > 1$. It means that Taylor representation (1) for $G(K)$ in the case of the $(HF)_2$ dimer is divergent for any $K \neq 0$. By neglecting the first two terms in the radicand (for $K \neq 0$) of $h(K)$ given by Eq. (7) we obtain the approximate relation for $h(K)$

$$h(K) = C_0 + C_1|K| + C_2\,K^2\,. \tag{12}$$

For the correction $\Delta h_1(K)$, associated with taking out the term $\Delta\tilde{A}(\rho)K^2$ into the perturbation for the ground state ($n = 0$), we may obtain the relation

$$\Delta h_1(K) = <\Psi_0|\Delta A(\rho)\,K^2|\Psi_0> = a_2\left(\frac{b_2}{\mu}\right)^{1/4}\frac{\Gamma\,(2S + 1)}{\Gamma\left(2S + \frac{3}{2}\right)}K^2\,,$$

where

$$S = \frac{1}{4}\left\{-1 + \sqrt{1 + 4\,(b_1 + a_1K^2)/\mu}\right\}\,,$$

and $\Gamma(\ldots)$ is the gamma–function. The use of asymptotic representation for the Γ–function and the approximate representation for $S \mid C_0 + C_1|K|$, yelds for the correction $\Delta h_1(K)$ the relation

$$\Delta h_1(K) \simeq \frac{C_2K^2}{\left(1 + C_3\,|K|\right)^{1/2}}\,. \tag{13}$$

Taking into account this correction for $h(K)$ in Eq. (12), we can represent the function $F(K)$ in the form

$$F(K) = h(K) + \Delta h_1(K) = C_1\,|K| + \frac{C_2K^2}{\left(1 + C_3\,|K|\,\right)^{1/2}}\,. \tag{14}$$

It should be noted that the potential function $\tilde{V}_0(\rho) = b_0 + b_1/\rho + b_2/\rho^2$ also assumes an analytical representation[10] for $h(K)$ and results in the other form of $G(K)$. The retrieval of vibrational frequencies by employing the function $\tilde{V}_0(\rho)$ of the above type is worse than that with the potential function $V_0(\rho)$ given by Eq. (6), therefore, the solution $h(K)$ obtained from Eq. (4) with $\tilde{V}_0(\rho)$ is not considered in the paper.

A TWO–DIMENSIONAL CASE

Let us show briefly the possibility of considering the strong vibrational–rotational interaction in the $(HF)_2$ dimer for the case of the two vibrational coordinates. The coordinate $\rho = (\theta_1 + \theta_2)/2$ is defined in Ref. 1 in the form of a half–sum of two coordinates θ_1 and θ_2 specifying the changes of the angles between the bonds HF and the line joining the centroids of the HF molecules. In these variables Eq. (4) takes the form

$$\left\{-\mu\,\frac{\partial^2}{\partial\theta_1^2} - \mu\,\frac{\partial^2}{\partial\theta_2^2} + V_0\,(\theta_1, \theta_2) + \tilde{A}\,(\theta_1, \theta_2)\,K^2\right\}\Psi = h(K)\,\Psi. \tag{15}$$

The potential function

$$V_0\,(\theta_1, \theta_2) = \mathrm{b}\,(\theta_1^2 + \theta_2^2)$$

and the model representation

$$\tilde{A}\,(\theta_1, \theta_2) = a_0 + \frac{a_1}{\theta_1^2 + \theta_2^2}$$

assumes the solution of Eq. (15) in the form[15]

$$h(K) = \omega\,(|M(K)| + 1 + 2n_p), \tag{16}$$

where $M^2(K) = M^2 + (a_1/\mu)\,K^2$, $M = 0, \pm 1, \pm 2, \ldots$, and n_p is the principal vibrational quantum number. For the ground state $n_p = 0$ and $M = 0$, and from Eq. (16) it follows

$$h(K) = C_0 + C_1|K| + C_2 K^2$$

which coincides with Eq. (12). It should be noted that the representation $V_0(\theta_1, \theta_2)$ is approximate and assumes the presence of a minimum in the potential function of linear molecule.

SOLUTION OF INVERSE PROBLEMS

The functions $F(K)$ given by Eqs. (11), (12), and (14) were employed for fitting the experimental values of $F(K)$ given in Refs. 1 and 3 (for the hypothetical level $J = 0$). The results of solution of inverse problems are given in Table II along with their comparison with the results obtained with polynomial representation (1) and some fraction–rational forms of $F(K)$. It can be clearly seen that nonpolynomial representations (11) and (14) of $F(K)$ substantially improve the quality of retrieval and prediction of the molecular vibrational energy in comparison with the conventional power–law dependence (1) and with the fraction–rational dependences of $F(K)$.

TABLE II. Comparison between the quality of retrieval and prediction of the rotational energy $F(K)$ of the $(\mathrm{HF})_2$ *molecule (for hypothetical level $J = 0$) for different representations of $F(K)$ ($V = 1$, cm^{-1}) (against the criterion* $\delta F(K) = \max|F^{\mathrm{calc}}(K) - F^{\mathrm{exp}}(K)|$).

Representation of $F(K)$	L	$\delta F(K)$, $M = 3$ $K \le 3$	Prediction of $F(4)$ $F(4)^{\mathrm{exp}} = 386.7$	$\delta F(K)$, $M = 4$ $K \le 4$	Prediction of $F(5)$
$F(K) = C_2K^2 + C_4K^4$	2	3.9	339.2	6.2	518.8
$F(K) = C_1\|K\| + C_2K^2$	2	1.4	398.8	3.5	581.1
$F(K) = \dfrac{C_1K^2}{1 + C_2K^2}$	2	3.4	358.7	5.5	535.8
$F(K) = G + g_2G^2$	2	0.36	388.6	$\underline{0.5}$	571.0
$F(K) = C_2K^2 + C_4K^4 + C_6K^6$	3	0.0	604.6	3.1	667.8
$F(K) = C_1\|K\| + C_2K^2 + C_3K^3$	3	0.0	382.5	0.4	560.5
$F(K) = \dfrac{C_1K^2}{1 + C_2K^2 + C_3K^4}$	3	0.0	515.9	2.4	627.7
$F(K) = \dfrac{C_1K^2 + C_2K^4}{1 + C_3K^2}$	3	0.0	395.5	1.4	576.4
$F(K) = \dfrac{C_1\|K\| + C_2K^2}{(1 + C_3K)^{1/2}}$	3	0.0	385.8	$\underline{0.1}$	564.3
$F(K) = G + g_2G^2 + g_3G^3$	3	0.0	393.5	0.4	568.7
$F(K) = \dfrac{G + C_2K^2}{(1 + C_3\|K\|^{1/2})}$	3	0.0	388.1	0.1	565.7

Note: L is the number of adjustable parameters, M is the number of experimental values of $F(K)$ according to Refs. 1 and 3. $F(K)$ was predicted with the use of the parameters C obtained by fitting the experimental data on $F(0)$, $F(1)$, ..., $F(K - 1)$. The $\delta F(K)$ values are underlined for the best two– and three–parametric functions.

Further study will be based on the use of the determined functions $F(K)$ for describing the experimental inversion–rotational transition frequencies.

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