METHOD OF INTRAMOLECULAR INTERACTION THEORY IN SPECTROSCOPY OF NONRIGID MOLECULES

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A brief review is given of theoretical analysis of vibration–rotation spectra of nonrigid molecules. The work was done in the Laboratory of Theoretical Spectroscopy at the Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences. Particular emphasis is placed on H_2X–type molecules with the large–amplitude bending vibration and on H_3X–type molecules with inversion.

INTRODUCTION

Method of molecular spectroscopy have found a wide utility in various areas of knowledge. Vibration–rotation (VR) molecular spectra reflect the structure of molecules and the pattern of intra– and intermolecular interactions. These spectra are extensively used in modern chemistry and molecular physics. The study of VR spectra is of great importance to the solution of a number of problems in astronomy, meteorology, atmospheric optics, etc.

Nonrigid molecules have attracted close attention both from the theoretical and experimental standpoints. Interest in this type of molecules derives, on the one hand, from their role in nature (it will suffice to mention the H_2O molecule largely responsible for the infrared absorption of solar radiation in the Earth's atmosphere) and from a number of interesting fundamental problems faced with in the studies of these molecular spectra, on the other.

What molecules must be taken as nonrigid? Among these are generally the molecules for which approximations based on the solution of the harmonic oscillator and rigid rotator problems are liable to break down. From this standpoint, virtually all polyatomic molecules in the highly excited VR state must be taken as nonrigid. For a number of molecules, however, the approximations mentioned above fail even with low–lying VR states, which is related to one large–amplitude vibration or more within the molecule, or else to strong interactions between vibrational and rotational motions. Among these molecules are, first and foremost, light triatomic H_2X–type molecules (H_2O, CH_2, H_2S, etc.), wherein the H atoms are apt to execute vibrations, quasi–linear molecules (HNNN, HNCO, HCHO ...), wherein the end atom (as a rule, the light hydrogen atom) is in large–amplitude motion relative to the linear (or "nearly" linear) configuration of the molecule, and H_2S_2, H_2O_2 and N_2H_2 molecules, etc.

In this regard the most familiar example is the ammonia molecule (NH_3) wherein the nitrogen atom penetrates through a plane formed by the hydrogen atoms. As this takes place, the molecule turns from one configuration to another. Other representatives of this type of molecules are H_3O^+, CH_3^+ and SiH_3 ... .

A broad class of nonrigid molecules comprises molecules with internal rotation wherein one group of atoms is rotating relative to another CH_3NH_2,

CH_3OH ...) molecules with ring puckering vibrations ($O(CH_2)_3$ ...) .

Finally, structural nonrigidity of the molecule is an intrinsic property of dimers and molecular complexes wherein individual molecules are virtually free to move relative to each other (($HF)_2$, $(H_2O)_2$, ...). In a number of molecules there occur different types of large–amplitude vibrations. A case in point is the methanol molecule, CH_3OH, wherein the CH_3 group is rotating and the end H atom is moving relative to the symmetric configuration of the molecule. The intramolecular motions are determined by the form of the potential energy surface where the minimum is not distinct (for molecules with "floppy" bending vibrations, see Figure 1a) or there are several minima. The number of minima on the potential surface is determined by the number of possible molecular configurations realized in the course of a large–amplitude vibration. By way of illustration Figure 1b presents the cross section of the potential surface of the molecule of the ammonia type along ρ–coordinate which describes the inversion.
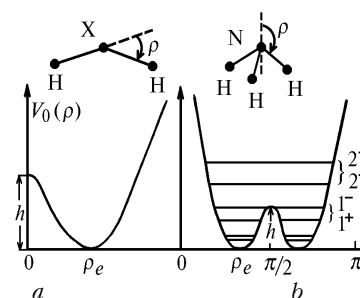

FIG. 1. Cross section of potential surface for nonrigid molecules of H_2O–type (a) and for molecules with inversion of NH_3–type (b) along the ρ–coordinate for large–amplitude vibration

Our interest in nonrigid molecules is primarily due to the light H_2X or H_2X–type molecules found among the constituents of the Earth's atmosphere or its pollutants. Regular inquiries into the problems involved in the interpretation of spectra of those molecules began in the late 1970s due to strong support of academician V.E. Zuev.

The paper gives a brief review of investigations conducted in the Laboratory of Theoretical Spectroscopy

at the Institute of Atmospheric Optics (IAO) of the Siberian Branch of the Russian Academy of Sciences.

1. PROBLEMS INVOLVED IN INTERPRETATION OF NONRIGID MOLECULAR SPECTRA

The most commonly used analysis of VR molecular spectra relies on the effective rotational Hamiltonian H with parameters (spectroscopic constants) chosen so as to provide the best fit to experimental data.[1–7, 45, 46] The application of this kind of Hamiltonians to VR spectra of nonrigid molecules leads to the following problems:

1. Spectroscopic constants depend crucially on quantum numbers associated with large–amplitude vibrations. Figure 2 depicts the behavior of experimental data[4–7] for centrifugal distortion constants of H_2O under excitation of a quantum number $n = v_2$. The shaded region shows the location of the constants for typical semirigid molecules. The tunnel effect exhibited by molecules with inversion results in the fact that the rotational structure of the energy levels of individual split components tends to be different. This manifests itself in essentially different spectroscopic parameters relevant to symmetric (s) or antisymmetric (a) (relative to the inversion operation) components. The difference may be as great as the proper values of the constants. This is the case, for instance, with the ammonia molecule.[8, 9] A dependence of this sort poses the following problem of practical importance: In what way can the information on the low–lying vibrational states be used to predict the rotational structure of the energy levels of the high–vibrational states?
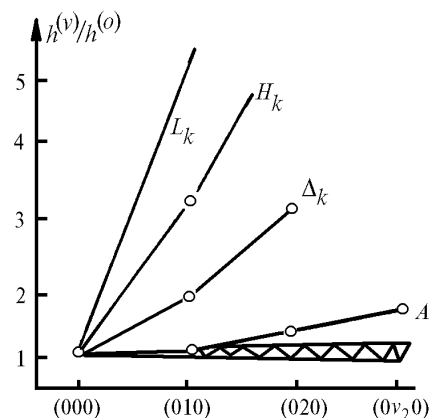
FIG. 2. *Vibrational dependence of centrifugal distortion constants for* H_2O. *The shaded region shows the permissible range of values for these parameters according to a conventional scheme.*

2. Nonrigid H_2X–type molecules in highly excited rotational states (with high rotational quantum numbers J and K) exhibit abnormal behavior. This shows up in the divergence of the commonly used effective Hamiltonians. Thus, to fit the energy levels of H_2O with $K_a \le 15$ the molecular Hamiltonian must incorporate terms which would normally correspond to tenth– and twelfth –order perturbation theory.[4] This introduces large errors into the calculated positions of spectral lines. Figure 3 gives indication of the spectroscopic information available for H_2O and depicts the behavior of the radius of convergence R_k (with respect to the quantum number K) depending on the vibrational state. A standard model of the Hamiltonian

is useful but only for description of the convergence domain for that Hamiltonian (the shaded region).
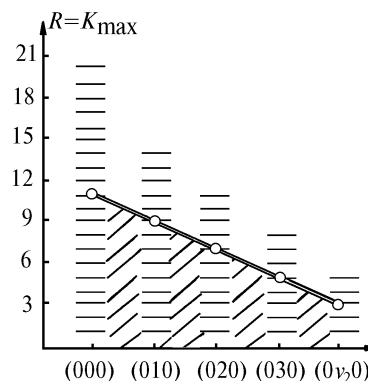
FIG. 3. *The currently available data for the water molecule (shown by horizontal lines) and the behavior of the radius of convergence commonly employed for prediction of these data by means of the effective rotational Hamiltonian* H_w.). *The shaded region shows the convergence domain for this Hamiltonian.*

The issues outlined above are essential to the problems of atmospheric optics where use is made of spectroscopic data banks. The latter inevitably invoke theoretical predictions and synthetic spectra. Figure 4 furnishes an example of a comparison between positions of experimental spectral lines[10] for H_2O and those predicted by standard Hamiltonian models (shown as starred lines). The calculated values have been entered into much used spectral data banks known as HITRAH and GEISA. This means that limitations of currently existing theoretical models may introduce serious errors in the interpretation of atmospheric measurements.
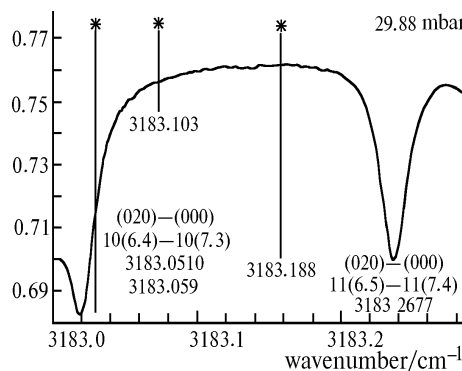
FIG. 4. *Comparison of experimental absorption line positions for* H_2O *reported in Ref. 10 with those listed in HITRAN and GEISA data banks.*

2. SEPARATION OF THE VIBRATIONAL VARIABLES AND THE EFFECTIVE HAMILTONIANS FOR NONRIGID MOLECULES

From the above discussion it is apparent that the VR Hamiltonian H for a nonrigid molecule is generally dependent on the coordinate of a large–amplitude vibration designated as ρ to distinguish it from the coordinates q_j for small–amplitude harmonic vibrations. Thus we have

$$H = H(q_i, \, p_j = -\,i\,\partial \,/\, \partial q_j; \; \rho, \, J_\rho = -\,i\partial \,/\, \partial\rho; \; J_x, \, J_{y'} \, J_z) \,. \quad (2.1)$$

In Eq. (2.1) J_α ($\alpha = x, \, y, \, z$) are components of the angular momentum operator along the molecular axes system. An exact expression for the quantum—mechanical operator H (Hougen—Bunker—Johns (HBJ) Hamiltonian) was derived in Refs. 11, 12.

The basic idea of the outlined approach is that (i) the transformation of H into the effective Hamiltonian H_{eff} must account for all peculiarities of the potential molecular function even in zero—order approximation and (ii) no expansion in terms of the coordinate of the large—amplitude vibration ρ is performed. This means that in the transformation scheme

$$H \rightarrow H \qquad\qquad\qquad (2.2)$$

a zero—order approximation H_0 incorporates, in addition to the harmonic vibration Hamiltonian $H_0^{\text{small vib.}}$, the Hamiltonian $H_0^{\text{large vib.}}$ for a large—amplitude vibration, i.e. $H_0 = H_0^{\text{small vib.}} + H_0^{\text{large vib.}}$, with

$$H_0^{\text{small vib.}} = 1/2 \sum_j \omega_j \, (\, p_j^2 + q_j^2);$$

$$H_0^{\text{large vib.}} = -\,\mu(\rho)\,\frac{\partial^2}{\partial r^2} + V_0(\rho) \,. \qquad (2.3)$$

It is to be noted that should the Hamiltonian H exhibit poor convergence in the angular momentum operators, a zero—order approximation must involve a term for the most complete description of the intramolecular torsion—rotation interaction. By a torsion variable is meant any one variable that describes a nonrigid vibration. This point is considered at length in later sections.

The transformation of Eq. (2.2) has been much studied for normal "semirigid" molecules and rested on the exact solution of the problem on a harmonic oscillator. For the Hamiltonian $H_0^{\text{large vib.}}$ the exact solution of the problem

$$H_0^{\text{large vib.}} \, \psi_n(\rho) = E_n \, \psi_n(\rho) \qquad (2.4)$$

remains unknown. Because of this, realization of the scheme given by Eq. (2.2) calls for special mathematical methods. Contact transformations (CT) expressed in terms of superoperators derived in Refs. 13—15 are the tool best suited for the job. This representation allows CT to be performed for any zero—order approximation adopted. Following the general CT scheme[13–15] the Hamiltonian H of Eq. (2.1) undergoes a series of CT to yield:

$$\tilde{H} = e^{-\,iS} \, H \, e^{iS} = \sum_{n \, v} P_{vn} \, H^{(n)} \, P_{vn} \,. \qquad (2.5)$$

If the state for which the effective Hamiltonian is constructed is not resonant with other states the transformed Hamiltonian $\tilde{H}$ must satisfy the requirement $[\tilde{H}, \, H_0] = 0$. This is equivalent to $\tilde{H}$ being diagonal with respect to the principal vibrational numbers v_j and n. The purpose that is served by the transformation of Eq. (2.5) is to eliminate from the original Hamiltonian all the terms $P_{v'n'} \, H^{(n)} \, P_{vn}$ linking the non—degenerate states $(v'n')$ and (vn). In Eq. (2.5) $P_{vn} = |\, v \rangle\langle v| \times P_n$, $|\, v \rangle$ is the vibrational wave function that

describes a small—amplitude vibration and P_n are projectors on the torsional states. The meaning of the projectors depends on whether the spectrum of H_0 is non—degenerate or marked by degeneracies or quasi—degeneracies. Let us consider specific examples of derivation of effective Hamiltonians for different types of nonrigid molecules.

A. Effective rotational Hamiltonian for H_2X—type molecules

For these molecules the spectrum of $H_0^{\text{large vib.}} = H_0^{\text{bend.}}$ is nondegenerate and P_n are determined by a simple relation of the form $P_n = |\, n \rangle\langle n|$, where $|n\rangle = |\psi_n\rangle$. Transformation (2.5) results in the effective rotational Hamiltonian $H_{\text{rot.}}^{(n)}$ for each of the vibrational states $(v \, n) = (V)$ to give:

$$H_{\text{rot.}}^{(\,V)} = E^{(\,V)} + \sum_{x \, y \, z} \left\{ B_\alpha^{(\,V)} J_\alpha^2 + \right.$$
$$\left. + \; \frac{1}{4}\, \tau_{\alpha\beta\gamma\delta}^{(\,V)} J_\alpha J_\beta J_\gamma J_\delta + \theta_{\beta \, \gamma \, \delta \, \varepsilon \, \eta}^{(\,V)} \, J_\alpha J_\beta J_\gamma J_\delta J_\varepsilon J_\eta + \dots \right\}.$$
$$(2.6)$$

Eq. (2.6) has the same form as the one used for semirigid molecules, except that the relations linking the spectroscopic constants B, τ, ... with the potential and the inertia tensor are essentially different. For example, the formula for the major contribution of $\tau^{(n)}$ (v —independent) to the constant $\tau^{(V)}$ is of the form:[16]

$$\tau_{\alpha\beta\gamma\delta}^{(\,n)} = -\,2 \sum_{s \, k} \frac{B_\kappa^{\alpha\beta}(n \, s) \, B_\kappa^{\chi\delta}(s \, n)}{\omega_\kappa + \Omega_{s \, n}} - 4 \sum_{s \, \neq \, n} \frac{B_\alpha(n \, s) \, B_\beta(s \, n)}{\Omega_{s \, n}} \, \delta_{\alpha\beta} \delta_{\chi\delta} . \quad (2.7)$$

The most essential distinction between our approach and well—established concepts[1–4] lies in the fact that the major contributions to $B^{(n)}$, $\tau^{(n)}$, ... via the wave functions $\psi_n(\rho)$ depend heavily on the quantum number $n = v_2$. For a group of the resonating bending—vibrational states $(n \, v)$ and $(m \, v)$ the effective Hamiltonian takes the form:

$$H^{[n, \, v; \, m, \, v']} = \begin{pmatrix} H^{(n, \, v)} & h_{v \, v'}^{n \, m} \\ \text{H.C.} & H^{(m \, v)} \end{pmatrix}, \qquad (2.8)$$

where H.C. is the Hermitian conjugate part of the Hamiltonian. The form of the operators $h_{v \, v'}^{n \, m}$ is determined by the concrete type of resonant interactions, albeit the dependence of $h_{v \, v'}^{n \, m}$ on the rotation operators is similar to that adopted in the semirigid molecular model.[17–19] The effective Hamiltonians H can be reduced to an empirically reproducible form $\tilde{H}$ similarly to the semirigid molecular model.[45, 46, 64] Thus, for the isolated vibrational state (V) the Hamiltonian $\tilde{H}^{(V)}$ is of the form

$$\tilde{H} = H_W^{(V)} = \sum a_{ij}^{(V)} J^{2i} J_z^{2j} + \sum b_{ij}^{(V)} J^{2i} \left\{ J_z^{2j}, J_{xy}^2 \right\}. \qquad (2.9)$$

B. Effective Hamiltonian for H_3X—Type molecules with inversion

For molecules of this type the potential function in the Schrödinger equation (2.4) has two minima separated by a barrier (Figure 1b). The eigenfunctions are either totally symmetric: $|\psi_{n^+}\rangle = |\, n^+\rangle$, or antisymmetric: $|\psi_{n^-}\rangle = |\, n^-\rangle$

with respect to the inversion operation. The energies of the low—lying inversion states are quasi—degenerate. The projectors P_n have the form: $P_n = |n^+><n^+| + |n^-><n^-|$. Not counting accidental resonances where the inversion mode is resonant with other vibrations, the generalized CT technique provides transformation of Hamiltonian H of Eq. (2.1) to the effective Hamiltonian $H^{(n)}$ for a pair of states[20]:

$$H^{(n)} = \begin{pmatrix} H_{n^+ n^+} & H_{n^+ n^-} \\ \text{H.C.} & H_{n^- n^-} \end{pmatrix}. \qquad (2.10)$$

To put it differently, the Hamiltonian $H^{(n)}$ describes the rotational structure of the energy levels of the two quasi—degenerate states (n^+, n^-), $n = 0, 1, \ldots$. The expansion of the diagonal blocks $H_{n^+ n^+}$ and $H_{n^- n}$ has the form of Eq. (2.6). In this case the formulas for $B^{(n)}$, $\tau^{(n)}$ are still valid (here $n = 0^+$, 0^-, 1^+, ...). The form of the operators $H_{nn'}$ was discussed in Ref. 21. In the special case of modest inversion level splitting, the nondiagonal part $H_{n^+ n^-}$ can be eliminated by means of further transformation[20] so that the Hamiltonian $H^{(n)}$ breaks down into two pure rotational Hamiltonians $H^{(n^+)} = H_{n^+ n^+}$ and $H^{(n^-)} = H_{n^- n^-}$.

C. Effective Hamiltonian for CH_3OH—type molecules with internal rotation

For the methanol molecule CH_3OH the potential function $V_0(\rho)$ is sinusoidal in shape with a period $2\pi/3$. The wave function $|\psi_{n\sigma}> = |n, \sigma>$ is characterized by the principal torsion number n as well as by the index $\sigma = 0, 1, -1$ denoting symmetry or periodicity of the wave function. The projectors P_n have the form: $P_n = \sum_r |n, \sigma><n, \sigma|$. The effective Hamiltonian for a set of the torsion sublevels $|n, \sigma>$ assumes the matrix form:

$$H^{(n)} = \begin{pmatrix} H_{0\,0} & H_{0\,1} & H_{0\,-1} \\ & H_{1\,-1} & H_{1\,-1} \\ \text{H.C.} & & H_{-1\,-1} \end{pmatrix}. \qquad (2.11)$$

3. DEPENDENCE OF SPECTROSCOPIC PARAMETERS ON VIBRATIONAL QUANTUM NUMBERS CORRESPONDING TO "SOFT' BENDING VIBRATIONS OR INVERSION MOTIONS

Contrary to conventional formulas for the spectroscopic constants (SC) B, D, H adopted in the semirigid molecular model developed by Amat, Nielsen et al.[1–4] the relations derived in this work to link SC ($B^{(n)}$, $D^{(n)}$, $H^{(n)}$ and K and l doublings, etc.) with the molecular force field and inertia tensor take into account possible subbarrier tunnelling of the X atom in the H_3X—type molecules with inversion or linearization of the H_2X—type molecules. These relations depend on the barrier height h via the wave functions $\psi_n(\rho)$. Numerical calculations of the rotational $B_z = A$ and quartic Δ_κ constants for H_2O are demonstrated in Figures 5 a and b, respectively.[16,23,24] It is readily apparent from the curves that the rotational and quartic constants do depend critically on the bending quantum number $n = \nu_2$. Different slopes of the curves are attributed to the fact that different values of the parameter h governing the barrier height to the linear configuration are used in the potentials $V_0(\rho)$ adopted in the Schrödinger equation. To illustrate the behavior of the

centrifugal constants for the nonrigid H_2X—type molecules depending on the mass of the constituent atoms Figure 5c shows, as a case in point, the behavior of the quartic constant Δ_k for $H_2^{16}O$, $H_2^{18}O$, and $D_2^{16}O$, isotopes derived with the use of the same value of the potential $V_0(\rho)$. The curves make it clear that the heavier is the molecule, the weaker is the dependence of the centrifugal distortion parameters on the bending quantum number ν_2. Figure 5d presents calculated relationships for the rotational constant B_z of three nonrigid molecules H_2O, NH_2 and CH_2. The barrier h to the linear configuration for CH_2 is ~ 900 cm^{-1} (see Ref. 22).

Bending vibration modes introduce special features in the formation rules for polyads of resonating vibrational states in H_2X. Similar polyads occur in any one polyatomic molecule wherein there are certain relationships between fundamental vibration frequencies. Specifically, for H_2O the polyads of resonating states form according to the rule $2\nu_1 + 2\nu_3 + \nu_2 = p = 0, 1, 2, \ldots$, which follows immediately from the fulfilment of the relation $\omega_1 \cong \omega_3 \cong 2\omega_2$. It has been pointed out in the literature that with H_2O this rule is violated in some instances.[28,29] The results of calculations of different resonance parameters for H_2O (Fermi, Coriolis, etc.) are evidence for the existence of different resonances that bear no relation to the above conditions.[30] Figure 6a, b shows relationships between the resonance parameters F_0 and F_k for Fermi resonance and the vibrational state. It is evident that starting with some value of v_2 the resonance parameters $F_0(n, .n + 3)$ and $F_k(n, .n + 3)$, linking vibrational states from different polyads of resonating states, become comparable with the resonance parameters $F_0(n, .n + 2)$ and $F_k(n, .n + 2)$, linking states from the same polyad. By this is meant that a solution of the inverse spectroscopic problem, i.e. determination of SC from experimental data, must take into account the effect of the new resonance interactions.

The problem of evaluation of a relationship between SC and vibrational quantum number v_2 in H_2O also admits of an analytical solution found in Refs. 25–27. The dependence for SC $C_{lm}^{(n)}$ appearing in the reduced effective rotational Hamiltonian H_W of Eq. (2.9) before the operators J_z^{2l} is described by the relation:

$$C_{lm}^{(n)} = C_{lm}^{(0)} + (-1)^l \eta_m [A^{(n)} - A^{(0)}] (Y_n)^l, \qquad (3.1)$$

where the parameters n determine different subsequences in H_W, and $A^{(n)} - A^{(0)} = \gamma(n) \exp[a(n)]$, $Y_n = W \exp\{a_4 \, a(n)\}$. The functions $\gamma(n)$ and $a(n)$ may be expanded in a power series as:

$$\gamma(n) = \gamma_0 + \gamma_1 n + \ldots, \quad a(n) = a_1 n + a_2 n^2 + \ldots.$$

The relationships arrived at differ from the series expansion used for typical molecules and make possible the description of the majority of SC for H_2O in the (0, v_2, 0) ($v_2 = 0, 1, 2, 3, 4$) states with an average accuracy of 2–5%. Interestingly, Eq. (3.1) has the advantage whereby the operator $\Delta H^{(n)}$ describing to a first approximation the change in the rotational structure of the molecule with the excitation n may be written as

$$\Delta H^{(n)} = [A^{(n)} - A^{(0)}] \times$$

$$\times \left\{ \frac{J_z^2}{1 + Y_n J_z^2} + h_1 \frac{J^2 J_z^2}{1 + Y_n J_z^2} + h_2 \left[J_{xy}^2, \frac{J_z^2}{1 + Y_n J_z^2} \right] \right\}, \qquad (3.2)$$
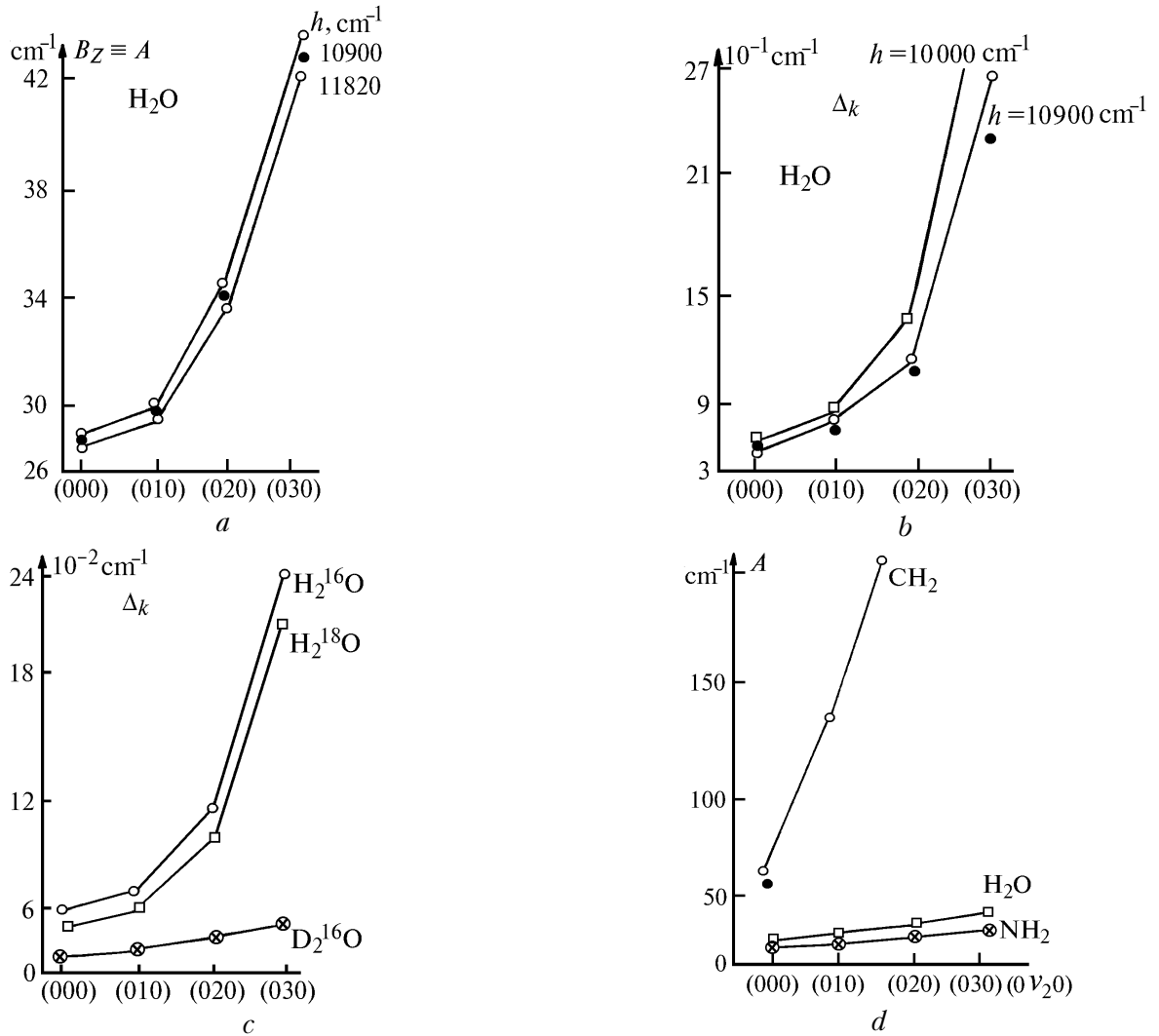
FIG. 5. Calculated (shown by open circles, squares and crosses) and experimental (shown by closed circles) relationships for rotational and quartic centrifugal distortion constants of H_2O (a, b, and c) and NH_2 and CH_2 (d)
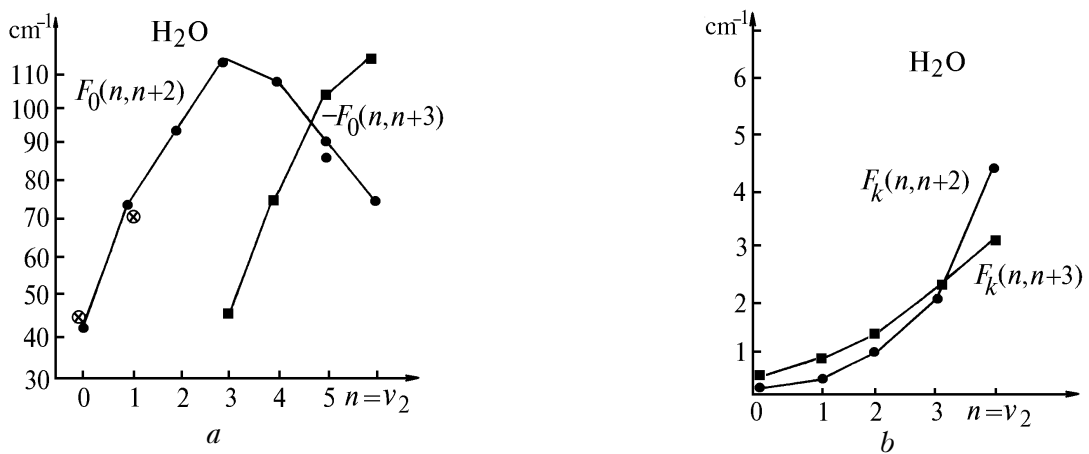

FIG. 6. Calculated dependence of the F_0 and F_k parameters of Fermi resonance on the vibrational state. The $F_0(n, m)$ and $F_k(n, m)$ parametrers describe the interaction between the states with the quantum numbers n and m.

To calculate $\Delta H^{(n)}$ we need only know six parameters: : γ_0, η_1, η_2, a_1, a_4, and W.

One of the most fascinating manifestations of nonrigidity in the centrifugal distortion of molecules with inversion is the experimentally observable difference in the rotational structure associated with the symmetric (s) and antisymmetric (a) sublevels of a particular vibrational level. The relationships derived here for SC take into account (via $\Psi_n(\rho)$) the dependence of SC on the barrier height h and, in the limiting case $h \to \infty$, tend to change to the relationships known from the literature for SC of normal semirigid molecules. The finiteness of the potential barrier and possibility of the X–atom tunnelling across the plane H_3 gives rise to new types of contributions to the centrifugal distortion that "suppress" conventional mechanisms responsible for the n–dependence of SC. Using the approach put forward here, these mechanisms can be considered in their own right by lowering h from ∞ to 0, which corresponds to a nominally continuous change from a semirigid molecule to a rigid one.

The calculations performed for the NH_3–type molecules[23, 31, 32] do show the occurence of nonequivalence of rotational structures as h is lowered while the remaining parameters are fixed.

Let us look at NH_3. For this molecule the true value of $h = h_{NH_3} \cong 2\,000$ cm^{-1} and the curves closely approximate the experimental values of the difference $D^a - D^s$. The nonequivalence is associated, in physical terms, with the fact that the parameters B^s and D^s undergo more dramatic changes in comparison with the slightly changing B^a and D^a (Figure 8) as n rises in the (0, 0, 0, 0), (0, 1, 0, 0), (0, 2, 0, 0) and (0, 3, 0, 0) states.
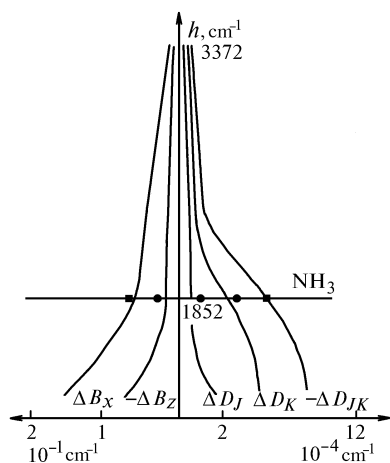

FIG. 7. The evolution of the differences $\Delta B = B^s - B^a$ and $\Delta D = D^s - D^a$ with lowering of the potential barrier h in the H_3X–type molecule with inversion (closed circles and squares illustrate experimental differences for the ammonia molecule).

The dominant mechanism responsible for maximum changes of B^s and D^s (see Figure 8) is delocalization of the N atom in potential wells for the s–states. The calculations of $|\psi_n(\rho)|^2$ show that the probability of the N atom being separated from the plane H_3 by a distance of 0.1 Å is an order of magnitude higher for the (0, 1^s, 0, 0) state than for the (0, 0^s, 0, 0) state by virtue of the subbarrier tunnelling. For the first above–barrier (0, 2^s, 0, 0) state this

probability increases ten times extra and the configuration is most likely to be plane. In this regard such configuration may be termed a new "equilibrium" configuration. In the a–states that mechanism is inoperative, because the probability of the plane configuration is zero for all $n = v_2$ and h. In the $n\,v_2$ states at $n > 2$, $\psi_n(\rho)$ oscillates progressively faster, the contributions from different configurations to effective inertia moments are averaged and the parameters B^s and B^a are bound to come closer in magnitude (Figure 8), which is in line with findings of Ref. 8, 9.

For D–parameters the major mechanism is decompensation of contributions from the interaction with the nearest levels. The contributions from the interaction with the upper (D_{upper}) and lower (D_{lower}) vibrational states of the same mode to the centrifugal distortion are opposite in sign. In the conventional theory of semirigid molecules (associated with $h = \infty$) $D_{upper} = $ const $(v + 1)$ and $D_{lower} = $ const $(-v)$, which results in compensation for v–dependence in the major contributions from $D_{upper} + D_{lower} \cong $ const. A decrease in h initiates much stronger perturbations of the subbarrier s–state (particularly the s–level next to the barrier) than the relevant a–states. This accounts for the behavior seen in D^s and D^a which are at their maximum for v_2 (Figure 9).
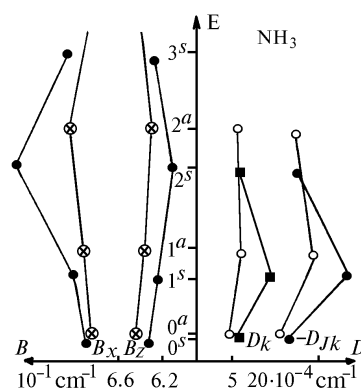

FIG. 8. Theoretical dependence of the B and D parameters on the energy of the inversion states
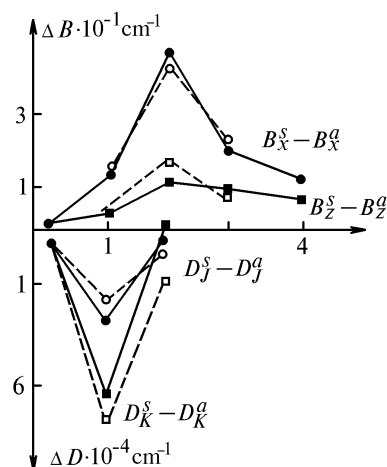

FIG. 9. The experimental (shown by open circles and squares) and calculated (shown by closed circles and squares) differences $\Delta B = B^s - B^a$ and $\Delta D = D^s - D^a$ vs. the quantum number v_2 for NH_3.

These deductions are confirmed by similar calculations for the H_3O^+ ion wherein the distribution of inversion levels relative to the barrier is somewhar different from the one found for NH_3 (see Refs. 33–36). In that instance the maximum difference in the rotational constants $|B^s - B^a|$ is observed for the ν_2 state, whereas the maximum difference $|D^s - D^a|$ occurs for the ground inversion state.

4. GENERATING FUNCTIONS FOR EFFECTIVE ROTATIONAL HAMILTONIAN OF H_2O–TYPE NONRIGID MOLECULES

The theory of generating functions has been developed because of the need for a highly accurate description and prediction of excited rotational states of the water molecule. For the ground molecular state the rotational energy levels derived from experimental data involve the rotational quantum numbers $J \le 35$, $K_a \le 20$ (see Ref. 37). While this information has been known since 1976, it was not until recently when an adequate theoretical treatment of a complete set of the revelant data made its appearance. First and foremost this is due to the fact that fitting of the rotational energy levels by means of standard rotational Hamiltonians loses its physical meaning starting with some value of the quantum number K in excess of the radius of convergence for this Hamiltonian. The effective rotational Hamiltonian H_{rot} in terms of the generating functions F and χ is of the form

$$H_{rot} = F(J^2, J_z) + 1/2 \left\{ (J_+^2 + J_-^2) \chi(J^2, J_z) + \chi(J^2, J_z)(J_+^2 J_-^2) \right\}$$
(4.1)

which is equivalent to

$$H_{rot}^{[J]} = F^{[J]}(J_z) + 1/2 \left\{ (J_+^2 + J_-^2) \chi^{[J]}(J_z^2) + \chi^{[J]}(J_z)(J_+^2 + J_-^2) \right\}.$$

for fixed J.

The functions F and χ are referred to as generating functions for the standard Watson Hamiltonian H_W (Eq. (2.9)), for their expansion into a Taylor series in the convergence domain results in expansion of H_{rot} whose form is identical to H_W of Eq. (2.9) and the expansion coefficients reproduce the values of SC for the Hamiltonian H_W.

The procedure adopted for derivation of the generating functions rests on the insertion of the operator $\tilde{h}(\rho, J)$ into the zero approximation $H_0^{large\ vib.} = H_0^{bend.}$ to provide a most complete description of the bending–rotational molecular interaction. In doing so, one has to proceed as follows:

1) For the Schrödinger equation

$$'H_0^{ben} \psi_n(\rho) = E_n \psi_n(\rho), \qquad 'H_0^{ben} = -\hat{B} \frac{\partial^2}{\partial r^2} + V_0(\rho), \quad (4.2)$$

where $\hat{B} = \frac{1}{\pi} \int_0^p \mu(\rho)\, d\rho$ and the potential function $V_0(\rho)$ is chosen so that its form admits of an analytical solution of Eq. (4.2). The parameters of the potential function $V_0(\rho)$ are chosen so as to provide the best reproduction of the large–amplitude vibration frequency $\Omega_{n0} = E_n - E_0$.

2) The inverse inertia tensors $B_\alpha(\rho)$ ($\alpha = x, y, z$) are modeled by the functions $\tilde{B}_\alpha(\rho)$

$$B_\alpha(\rho) \to \tilde{B}_\alpha(\rho), \qquad (4.3)$$

chosen so that their behavior is qualitatively the same both for $\rho \to \pi$, 0, and $\tilde{B}_\alpha(\rho)$ and makes possible an analytical solution of the equation

$$\left\{ 'H_0^{ben} + \tilde{h}(\rho, J) \right\} \psi_n(\rho, J^2, J_z^2) = h_n(J^2, J_z^2)\, \psi_n(\rho, J^2, J_z^2), \quad (4.4)$$

where

$$\tilde{h}(\rho, J) = \tilde{A}(\rho)\, J_z^2 + \tilde{B}(\rho)\, J^2,$$

for the operator $h_n(J^2, J_z^2)$ and functions $\psi_n(\rho, J^2, J_z^2)$.

The operators h_n and the functions ψ_n are parametrically dependent on the angular momentum operators J^2 и J_z^2, such as in the Born–Oppenheimer equation the potential W_e and the electron wave functions ψ_e are parametrically dependent on the internuclear coordinate operator R. Equation (4.4) is not an eigenvalue equation; the only dynamical variable is ρ. The major contribution of the effective rotational Hamiltonian to be symbolized by F_0 to the generating function F may be represented in terms of the operators h via the relation (the subscript n is dropped):

$$F_0 = h(J^2, J_z^2) - h(J = 0) = E^{(J)} + \gamma^{(J)} G(J^2, J_z^2).$$

The effective rotational Hamiltonian H_G based on the generating function may be written as:

$$H_G = {}^{diag.}H_G + {}^{n.diag.}H_G, \qquad (4.5)$$

where

$${}^{diag.}H_G = \sum_{i \hat{} 0} \gamma_i^{(J)} G^i, \qquad {}^{n.diag.}H_G = \sum_{r+j \ge 0} \gamma_{rj} J^{2r} \left\{ G^j, J_{xy}^2 \right\}.$$

Different operator forms for $G(J^2, J_z^2)$ are derived from the potential $V_0(\rho)$ for different representations of the functions $f(\rho)$ and $\phi(\rho)$

$$V_0(\rho) = C_0 + C_1 f(\rho) + C_2 \phi(\rho), \qquad (4.6)$$

with the model functions $\tilde{B}_\alpha(\rho)$ being built by means of the functions $f(\rho)$ and $\phi(\rho)$. Thus for $f(\rho) = 1/\rho^2$, $\phi(\rho) = \rho^2$ the G operator may be written as[39,40]

$$G = \frac{2}{\alpha^{(J)}} \left(\sqrt{1 + \alpha^{(J)} J_z^2} - 1 \right). \qquad (4.7)$$

The functions $E^{(J)}$, $\gamma^{(J)}$, $\alpha^{(J)}$ of Eqs. (4.5) and (4.7) admit of a series expansion in terms of the operator J^2. For instance,

$$E^{(J)} = E^{(0)} + E^{(1)} J^2 + E^{(2)} J^4 + \dots. \qquad (4.8)$$

The series expansions generally exhibit good convergence. For $f(\rho) = th\alpha(\rho - \rho_e)$, $\phi(\rho) = f(\rho)^2$ the generating function F may be represented as[38, 41]

$$F = \mu_1^{(J)} G + \frac{\mu_2^{(J)} G + \mu_3^{(J)} G^2 + \dots}{1 + \eta_1^{(J)} G + \eta_2^{(J)} G^2}. \qquad (4.9)$$

The procedure used for the construction of the generating function admits of the generalization based on

the insertion in the zeroth approximation of Eq. (4.2) of the following terms:

$$\tilde{W}_M(\rho, J) = \sum_{i=0}^{M} \tilde{w}_i^{(J)}(\rho) \, J_z^{2\,i} \,, \tag{4.10}$$

which involve powers of the operator[43] J_z^2. Specifically, for the potential $V_0(\rho) = \dfrac{C_1}{\rho^2} + C_1 \rho^2$ the G operator may be expressed in terms of the J—dependent parameters $\alpha_n^{(J)}$ as

$$G(M) = \frac{2}{\alpha_1^{(J)}} \left\{ \sqrt{1 + \sum_{n=1}^{M} \alpha_n^{(J)} J_z^{2\,n}} - 1 \right\} , \tag{4.11}$$

This form of $G(M)$ can be regarded as a generalization of the generating G function given by Eq. (4.7). A great number of examples offered in Refs. (38—44) demonstrate that the employment of the generating functions improves the quality of fitting of the experimental data by an order of magnitude (relative to the standard deviation χ) as compared to the polynomial Hamiltonian. In some instances the quality is improved by several fold as compared to the Pade—type Hamiltonian. A typical example is given in Tables I and II (Ref. 43) that list statistical characteristics and maximum uncertainties $\Delta E_{max} = \max |E^{cal} - E^{exp}|$ incurred in the reproduction of experimental data on the water molecule.

TABLE I. *Standard deviation* χ *of rotational energies of* H_2O *reproduced with different forms of effective rotational Hamiltonian (* $J \le 10$*, and* L *is the number of variable parameters).*

Hamiltonian model	L	Vibrational state			
		(0, 0, 0)	(0, 1, 0)	(0, 2, 0)	(0, 3, 0)
Polynomial H_W	15	64	153	104	55
Pade $H[2/1; 1/1]$	15	10	35	—	—
Generating function H_G	15	4	10	11	3.4

Note that fitting was performed up to sextic terms with

$$\chi = \sqrt{\left\{ \sum_{i=1}^{I} [(E_i^{cal} - E_i^{exp}) / \delta_i]^2 \right\} / (I - L)} \,,$$

where δ_i is the experimental measurement error. In the case of unweighted data processing by means of least squares fitting the calculation accuracy is characterized by mean deviation σ determined by the formula $\sigma = \sqrt{\Sigma / (I - L)}$, where Σ is the sum of squared ddeviations $\Sigma = \sum_{i=1}^{I} (E_i^{cal} - E_i^{exp})^2$ of the calculated data E_i^{cal} from the experimental measurements E_i^{exp} and I is the number of experimental energy levels.

TABLE II. *Statistical characteristics and maximum errors* ΔE_{max} *in description of experimental VR energy levels of water molecule*[43] *(sampled data with* L *designating the number of variable parameters)*

Characteristics	Vibrational (0, 0, 0) state, 121 energy levels up to $J, K \le 10$	
	Generating function H_G	Polynomial H_W
Σ cm^{-2}	$2.1 \cdot 10^{-3}$	$5.1 \cdot 10^{-1}$
σ, cm^{-1}	0.0045	0,071
ΔE_{max}, cm^{-1}	0.013	0.252
$\Delta E = |E^{cal} - E^{exp}| < 0.010$	96 %	16 %
$0.010 < \Delta E < 0.015$	4 %	7 %
$0.015 < \Delta E < 0.050$	—	15 %
$0.050 < \Delta E < 0.300$	—	42 %
L	13	15

5. THE STATE OF THE ART OF THE THEORY AND CALCULATIONS OF VR ENERGIES AND SPECTRA OF H₂O IN THE INFRARED REGION

Water vapor is a major absorbing species of infrared radiation in the atmosphere. In the most extensively employed spectroscopic data banks HITRAH and GEISA H_2O is classified as molecule No.1 according to its significance for investigations into atmospheric optics. This has motivated a stable interest in the theoretical and experimental study of H_2O spectra (see, for example, Refs. 4—7, 47—55 and references cited therein). By now the rotational structure of more than 120 bands for some ten isotopic species has been found experimentally at different values of pressure, optical thickness, temperature, and spectral resolution. In addition, transitions from superexcited rotational states have been measured in flame spectra with $T = 3\,000$ K, which made possible experimental determination of pure rotational levels up to 11 000 cm^{-1} (Ref. 37), ten times as large as the energy of fundamental vibrations and very nearly equal to the energy of the potential barrier to the linear configuration of the molecule. Due to a large body of experimental evidence available and pronounced effects of nonrigidity, H_2O has become something of a touchstone for a great number of models.[38—43,48—55,62—63,65] We recognize the following historically established general avenues of inquiry into the theory of VR spectra of the H_2O—type nonrigid molecules.

A. Polynomial model. Starting with classical investigations of Amat, Nielsen and Watson et al.[1—4,45,46] a conventional theoretical model has been based on the effective Hamiltonian H_W. For individual vibrational states, H_W is pure rotational and has the form of a power series expansion of the rotational energy operators in terms of the operators of the angular momentum components J_α (Eq. (2.9)). Flaud and Camy—Peyret[17,18]

extended the model to the interacting resonant states by incorporating an explicit form of "resonant blocks" in the polynomial form. The majority of papers devoted to interpretation and fitting of H_2O spectra rely on that model.

As previously noted, the above model is of limited utility, the restriction being due to the radius of convergence of the power series expansion (see Figure 3). The quality of the calculations is degraded drastically as the quantum numbers K_a and v_2 are increased.

B. Rigid bender, semirigid bender, and nonrigid bender models. Because the approximations used in Model A were not adequately substantiated from the physical standpoint it was suggested that the idea of the effective rotational Hamiltonian be abandoned.[47–55] Instead, Hoy, Bunker, Landsberg, et al.[47–49] developed a set of more sophisticated models based on bending–rotation Hamiltonians. The best model of that series is the nonrigid bender (NRB) model that provides the Hamiltonian H_{NRB} (see Ref. 47). The initial approximations are more correct in physical terms than those of Model A. Unfortunately, the complexity of Model A and the lack of efficient parametrization gave no way of approaching the experimental accuracy along this line.

C. Calculations based on potential function in terms of ab initio potential surfaces and inverse spectroscopic problem.[51–54] There are also "mixed" models known from the literature. They combine separate elements from Models *A* and *B*, and specifically, employ Radau coordinates for the bending–rotation part and phenomenological effective parameters of the (A)–type simultaneously.[65]

Advantages: Physically substatiated consideration of intramolecular interactions; qualitative analysis of the entire set of vibrational states; concurrent allowance made for the vibration–rotation state distribution in different isotropic species.

Disadvantages: The calculations fail to approach the experimental accuracy, even though the overall picture is correct in a qualitative sense. For example, recent investigations[55] conducted within the framework of the "global processing" of 120 vibrational states of 10 isotopic species with energies $0 \leq E \leq 18\,300$ cm^{-1} up to $\Sigma(v_i) \leq 6$ and $J_{max} \leq 10$ have yielded a standard deviation of 0.24 cm^{-1}, which gives an idea of the average computation accuracy. This does furnish solid data for the molecular geometry and force field and yet the resulting accuracy is inadequate for applications pertaining to atmospheric optics.

D. Effective Hamiltonians with improved convergence. Here we recognize

— phenomenological models using Hamiltonians of Pade form,[57,59–63] Borel form,[58] or the form of rational fractions, optimized according to the Ritz variational principle;[56]

— models based on taking into account the specific character of bending–rotation interactions to yield generating functions.[38–43] The salient features of these models have been discussed in earlier sections.

Finally, let us review the current status of research into the problem of description of highly–excited rotational states of the water molecule.

A. Rotational energies. Pure rotational energy levels for the ground molecular state up to $11\,000$ cm^{-1} ($J \leq 35$, $K_a \leq 20$) were derived by Flaud and Camy–Peyret.[37] They found that the effective polynomial Hamiltonian H_W did not provide reasonable accuracy of the fit for the energy

levels with $K_a \geq 15$, even though it did involve terms with very high powers of angular momentum operators. The application of new methods (RB and NRB techniques, Borel method, etc.) was inefficient in fitting the highly excited rotational energies at $K_a \cong 20$ with an accuracy comparable to that obtained experimentally.

A substantial improvement in the quality of fitting those states was obtained in the Laboratory of Theoretical Spectroscopy at IAO. The very first applications of G functions in the form given by Eq. (4.7) with the terms up to G^3 enabled us to describe all energy levels up to $K_a \leq 20$ with an accuracy better than 1 cm^{-1} (Refs. 39, 40). In fitting the calculated data on 428 energy levels up to J, $K_a \leq 20$ to the experimental evidence the use of 26 parameters in the Hamiltonian H_G of Eq. (4.5) and the generating functions F and χ in the form of Eq. (4.9) resulted in the value of the sum of squared deviations $\Sigma = 1.43$ cm^{-2}, which corresponds to $\Delta E_{max} = 0.2$ cm^{-1} for $J = 20$ and $\sigma = 0,06$ cm^{-1}. The values of Σ, σ, and χ defining the quality of data fitting are listed in Table I. The calculations based on the use of the reduced form of Pade–approximant[61] furnished the same result. An extended set of 35 adjustable parameters in the Pade–approximant yields $\sigma = 0.03$ cm^{-1} and $\chi = 8.5$ (Refs. 59, 60). Recent "mixed" model for the molecular Hamiltonian developed in Ref. 65 has provided the same accuracy of the fit as the one reported in Refs. 59, 60 except for the energy levels with $J = K_a = 19$ and 20.

The results of the most accurate calculations based on the use of G functions are discussed in Ref. 68. For 560 experimental rotational levels of the ground state in H_2O χ was found to be 2.1 up to $J = 35$.

For comparison Table III includes energy levels with J, $K_a \leq 20$ calculated by different methods.

TABLE III. Rotational energies of H_2O up to J, $K \leq 20$ derived with different forms of effective rotational Hamiltonian.

Hamiltonian characteristics	Pade–type Hamiltonian * Ref. 60	Radau Hamiltonian * Ref. 65	G–function Ref. 66
χ	6.7	5.8	1.8
ΔE_{max} (cm^{-1})	0.16	0.347	0.034
ΔE_{max} (cm^{-1}, $J = 20$)	0.096	4.911	0.012
σ	0.03		0.007
L	35	39	37

* Except for $J = K_a = 19$ and $J = K_a = 20$.

B. The first and the second triads of resonant states. Until quite recently the energy levels, spectral line centers and intensities have been calculated from a conventional model for the effective Hamiltonian describing a polyad of resonating states.[5–7] New FTS measurements for H_2O between $2\,000$ and $6\,600$ cm^{-1} (the path length and pressure are 288 m and $\lesssim 30$ mbar respectively) have been performed by Keppler et al.[10] The spectrum has been identified and processed by means of the G function. Several hundreds of new experimental absorption lines with high quantum numbers J and K have been revealed.

C. The $n\nu_2$ states. Exploration of the series of bands ν_2, $2\nu_2$, ... is essential for a better insight into the intramolecular interactions, because the rigidity effects are dramatically enhanced as the "bending" mode is excited (Figure 3). "Global" calculations of rotational energies from the molecular potential[55] fall short of the accuracy which is needed for atmospheric applications. Of interest, then, is the use of the G functions for this purpose. It has been shown in Refs. 38−43 that calculations along these lines improve the quality of prediction (in terms of χ) by a factor of 2 to 3 over the Pade−models and by an order of magnitude over the polynomial models. A concurrent processing of the rotational $(0, v_2, 0)$ energies of the $(v_2 = 0, 1, ... , 4)$ states with the use of the G functions is given in Ref. 42. The application of the G functions to fitting new experimental FTS data presented a means of identifying and processing all transitions associated with the $4\nu_2$ band ($J \leq 13$, and $K_a \leq 5$) with $\sigma = 0.002$ cm^{-1}.

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