A NEW RESONANCE IN THE H₂O MOLECULE

A.D. Bykov, O.V. Naumenko, and L.N. Sinitsa

Institute of Atmospheric Optics,
Siberian Branch of the Academy of Sciences of the USSR, Tomsk
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The energy levels with $J \leq 5$ of the vibrational states which belong to the first decade of the resonating states of $H_2^{16}O$, are analyzed. The strong dependence of the nondiagonal matrix elements of the inverse inertia tensor b_{zz} on the coordinate of the bending vibration leads to a new type of the resonance, named HEL (highly excited local) resonance.
The HEL resonance couples the states highly excited over V_2 with $\Delta V_2 = \pm 5$, which belong to different resonance polyads, and is of a local character.

Water vapor plays an important role in atmospheric absorption of radiation in the optical range. In this connection, investigations of the peculiarities of the formation of the vibrational-rotational energy spectrum of the water molecule are of interest not only for specialists in the domain of the molecular spectroscopy, but also for those in the field of atmospheric physics.[1]

A number of new phenomena have been recently discovered in the vibrational-rotational dynamics of the water molecule. In some papers (see, e.g., Refs. 2 and 3) it was found that the vibrational-rotational interaction in a strong vibrational excitation could considerably transform the energy spectrum. Bending vibrations of large amplitude in the water molecule result in an anomalously rapid growth of the rotational and centrifugal constants[4–5] and the formation of a predissociation barrier with the excitation of the bending vibration.[6] A strong vibrational excitation is likely to result in new resonance effects as well.

The conventional scheme of constructing the effective rotational Hamiltonian for the polyads of the interacting vibrational states of the H₂O molecule assumes the presence of accidental resonances of three types:

— the Coriolis resonances for the states

V_1, V_2, V_3, and $V_1 \pm 1$, V_2, $V_3 \mp 1$;

V_1, V_2, V_3, and V_1, $V_2 \pm 2$, $V_3 \mp 1$;

— the Fermi resonances for the states

V_1, V_2, V_3, and $V_1 \pm 1$, $V_2 \mp 2$, V_3;

— the Darling-Dennison resonances for the states

$$V_1, V_2, V_3, \text{ and } V_1 \pm 2, V_2, V_3 \mp 2; \tag{1}$$

and some combinations of the above, as well.

At the same time, the Hamiltonian of H₂O-type molecules contains the term

$$b_{zz}(\theta)J_z^2 = \frac{b_{zz}^e}{1 + \cos\theta} J_z^2, \quad b_{zz}^e = \frac{\hbar^2}{2\mu r_e^2}, \tag{2}$$

which strongly depends on the θ coordinate describing a "large" bending vibration (θ is the angle between the OH bonds, μ is the reduced mass, and r_i is the equilibrium bond length).[6] As a consequence, in exciting one or several quanta of the bending vibration the nondiagonal matrix elements of the inverse inertia tensor $b_{zz}(\theta)$ can become considerable in magnitude (for $\theta \to \pi$, $b_{zz}(\theta) \to \infty$) and result in a break-down of the condition of applicability of the perturbation theory, i.e., in giving rise to new resonance interactions.

In this paper we have analyzed the energy structure of the first decade of H₂O and discovered that the anomalous dependence of the nondiagonal matrix elements b_{zz} on the bending vibration results in the formation of a new kind of resonance between the highly excited states of the H₂O molecule which is not associated with the ordinary resonances (1). The states listed in Table I belong to the first decade of the interacting states of H₂O. The vibrational-rotational energy levels for eight of them, marked by an asterisk, are given in Ref. 10. In order to solve the inverse problem for the first decade, it is necessary to take into account the states (060), (041), and (140), which correspond to a high degree of excitation of the bending vibration of large amplitude. It is well known[4,5] that calculation of the vibrational-rotational levels of these states requires the application of special procedures, since the matrix elements of the effective Hamiltonian, which is given in the form of the conventional power series, diverge even at small values of the quantum number K_a. As a consequence, we use the Pade-Borel method of approximants[11] to calculate the energy levels. In the calculation of the centers of the bands E_v, the inverse vibrational problem was solved anew. The formulas from Ref. 4 were applied to evaluate the rotational and centrifugal constant for state of the type (OV₂O), while the ordinary serial formulas were used for the other states. To evaluate the resonance constants, their values for the lower resonance polyads given in the literature and the well known formulas which describe their vibrational dependence[8] were used.

TABLE I. *Energies of the vibrational states of the* H_2O *molecule in the region* 1 μm, cm^{-1}.

V_1	V_2	V_3	E_v
0	0	3•	11032
1	0	2•	10869
2	0	1•	10613
3	0	0•	10600
0	2	2•	10522
1	2	1•	10329
2	2	0•	10284
0	4	1•	9834
1	4	0	9728
0	6	0	.8909
0	7	0	10205

TABLE II. *Reproduction of the energy levels of the state* (220) *without taking into account the HEL resonance (a) and with it (b),* cm^{-1}.

J	K_a	K_c	E^{exp}	$\Delta = E^{calc} - E^{exp}$	
				a	b
1	1	1	10324.80	1.27	-0.02
1	1	0	10330.73	1.17	-0.04
2	1	2	10365.17	1.25	0.03
2	1	1	10382.85	1.01	-0.01
3	1	3	10425.12	1.13	0.05
3	1	2	.10460.06	0.82	0
4	1	4	10504.03	0.90	0
4	1	3	10561.03	0.62	0
5	1	5	10601.27	0.58	-0.04

The solution of the inverse problem taking into account all the possible resonance interactions (1) as well as their combinations for the eight vibrational states listed in Table I (the energy levels up to $J = 5$ were used) showed the presence of a strong pertur- bation of the energy levels of the state (220) with $K_a = 1$. The exclusion of these levels from the fitting process makes it possible to determine a set of the rotational, centrifugal, and resonance constants for all the states (including (220)), the reproduction of the experimental data being in this case good.

At the same time, for the levels of the state (220) with $K_a = 1$, the calculated values of the energy levels deviate considerably from the experimental ones. These deviations are given in Table II. They can be explained by the presence of another resonance in- teraction between (220) and some vibrational state close to it. However, various ways of solving the inverse problem which take into account the resonance interactions within the decade do not allow us to explain the observed deviations, and the rotational perturbation of the levels with $K_a = 1$ should be

explained by an interaction with the states belonging to other resonance polyads of H_2O. Note that mixing of the levels of the states from different resonance polyads of water vapor ("quadruple" resonance) was observed earlier.[13,14]

The state (070), which belongs to the second decade of the resonating states, is close to (220) in energy. The centers of the bands (220) and (070) 'are shifted about 80 cm however, owing to a large value, of the rotational constant $A = 138$ cm^{-1} for (070); the energy levels with $K_a = 1$ turn out to be close. It can be seen that the resonance between the states (220) and (070) is determined by the nondiagonal matrix element of the inverse moment of inertia of the type

$$F_k^{V_2 V_2'} = \langle V_2 | b_{xz}(\theta) | V_2' \rangle \propto C\alpha^{V_2 + V_2'}. \qquad (3)$$
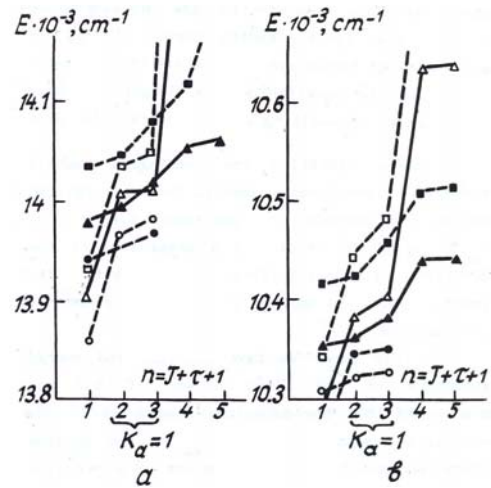

FIG. 1. *The local resonance of the levels with* $J = 1$ *(empty and filled circles),* $J = 2$ *(empty and filled triangles), and* $J = 3$ *(empty and filled squares) for the following highly excited states: a) (170) represented by the empty symbols and (122) given by the filled ones, b) (070) — by the empty and (220) — by the filled* ($\tau = K_a - K_c$).

Here C is a constant, $a = 12$, and F_k is the resonance constant. The estimator formula (3) was obtained by solving a model problem for the bending vibration of H_2O with the Pöschl–Teller potential, the potential parameters being taken from Ref. 12. As can be seen from Eq. (3), F_k increases rapidly as the vibrational quantum numbers of the bending vibration increase. Here, as a consequence of the proximity of the levels, the resonance corrections to the energy can become considerable already at the value of the resonance constant $F_k = 1$, which explains the ob- served perturbations. In Fig. 1 the energy levels for $J = 1$, 2, and 3 of the vibrational states (220) and (070) are plotted. It can be seen that only the mutual influence of the levels with $K_a = 1$ can be significant, the difference of the energy levels for $K = 0$, 2, and 3 being very great. As a consequence of the localizability

of the resonance, excluding the perturbed levels of the state (220) from the solution of the inverse problem, it turns out also to be possible not to take the state (070) into account and to solve the inverse problem neglecting the resonance interactions between them, as was done in Ref. 15 in an analysis of the states of the first decade of $H_2^{18}O$.

Consideration of the resonance between the vibrational states (220) and (070) makes it possible to explain completely the observed anomalies in the energy spectrum. The standard deviation is 0.014 cm^{-1}, the maximum deviation being 0.06 cm^{-1} for all the levels involved in the fit. The parameter set so determined was used to analyze the spectra of water vapor obtained from the Fourier spectrometer,[10] that made it possible to find three new energy levels of the state (022). These are 212 (energy 10602.9148 cm^{-1}), 313 (10663.4088 cm^{-1}), and 321 (10747.0466 cm^{-1}).

TABLE III. Prediction of the energy levels for the state (121) with J = 6 cm^{-1}.

J	K_a	K_c	E^{calc}	$\Delta = E^{calc} - E^{exp}$
6	0	6	10761.02	−0.02
6	1	6	10762.05	0
6	1	5	10872.36	0.01
6	2	5	10888.26	−0.05
6	2	4	10939.55	0.01
6	3	4	11005.40	0.14
6	3	3	11016.35	0.11
6	4	3	11140.14	0.07
6	4	2	11140.22	0.08
6	5	2	11301.25	0.04
6	5	1	11301.14	−0.01
6	6	1	11493.23	0.35
6	6	0	11493.24	0.22

The values of the spectroscopic constants obtained in the solution of the inverse problem agree well with the preliminary estimates and similar constants for the lower resonance polyads of H_2O. The constants possess a good predictive ability. Thus all the known experimental levels for $J = 6$ and $K_a \leq 5$ (65 values) are predicted with a mean error of 0.037 cm^{-1}. Predictions of the energy levels with $J = 6$ of the state (121) are given by way of an example in Table III. For higher values of J, as our estimates show, the presence of resonances between the states (201), (102), (300), (003), (150), and (051) is possible.

A diagram of the vibrational energy levels of H_2O is given in Fig. 2, from which it follows that a number of highly excited (with respect to V_2) vibrational levels turn out to be close in energy to the states of the lower resonance polyads, the resonances also being of a local character, as can be seen from Fig. 1a. The analysis of the states of the second hexad $2\nu + \delta$ shows that the perturbations produced, as in our case, by the

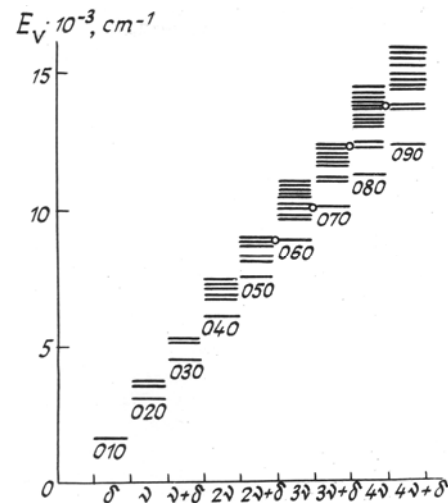interaction of the states (012) and (060) with $V_2 = 5$ and $V_3 = -2$ are observed in the energy spectrum.

FIG. 2. Diagram of the vibrational states of the H_2O molecule.

Our analysis of the energy structure of the polyads 4ν and $4\nu + \delta$ also indicates the possibility of resonance interactions of a new type. Thus, the new accidental resonance has a systematic character. Beginning with a certain vibrational energy it couples all the resonance polyads and should be taken into account in analyzing the absorption spectra and energy structure of highly excited vibrational-rotational states of the water molecule.

The found local resonance for the highly excited vibrational states is associated with a strong centrifugal effect, which manifests itself in the excitation of a bending vibration of large amplitude. It is due to the great magnitude of the matrix elements of the inverse moment of inertia. In this sense, the new resonance differs qualitatively from the accidental Coriolis, Dariing-Dennison, and Fermi resonances considered earlier and associated with the anharmonic and Coriolis constants. A new resonance couples the states with large variations of the vibrational quantum numbers

$$V_1, V_2, V_3, \text{ and } V_1 \pm 2, V_2 \mp 5, V_3,$$

$$V_1, V_2, V_3, \text{ and } V_1, V_2 \mp 5, V_3 \pm 2. \tag{4}$$

Mixing of the states V_1, V_2, V_3 and $V_1 \pm 1$, $V_2 \mp 5, V_3 \pm 1$ is also possible.

In accounting for the new accidental resonance, the scheme of constructing the resonance polyads for the water molecule is not valid. The highly excited vibrational states are effectively mixed together as a consequence of the strong centrifugal effect, forming the overall reservoir of vibrational states which determines the physical and chemical properties of the molecule.

Accounting for the peculiarities of the manifestation of this resonance, namely its local character

and its existence only for the highly excited states, it can be called HEL (highly excited local) resonance.

Similar resonance interactions associated with a strong centrifugal effect are likely to be between the highly excited states in isotope-substituted molecules of $H_2^{17}O$, $H_2^{18}O$, HDO, or in water-like molecules H_2S, H_2Se, etc., which possess a vibration of large amplitude.

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