STUDY OF THE FINE STRUCTURE OF THE VIBRATIONAL-ROTATIONAL SPECTRUM OF WATER VAPOR

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STUDY OF THE FINE STRUCTURE OF THE VIBRATIONAL-ROTATIONAL SPECTRUM OF WATER VAPOR

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1. A wide range of problems in atmospheric optics, meteorology, astrophysics, and optoelectronic engineering requires knowledge of the fine structure of the vibrational-rotational spectrum of water vapor (line positions, their intensities, and half-widths).

Experimental determination of these characteristics is at present impossible for most lines (^{1}). The first attempt at a theoretical analysis of the fine structure of the 2.7 μ band of H_2O was undertaken in work (^{2}), in which the positions of the line centers were taken from experiment, while in calculating intensities and half-widths the interaction of the vibrational and rotational terms of the molecule was taken into account inconsistently.

In our work a quantum-mechanical study of the fine structure of the vibrational-rotational spectrum of water vapor has been carried out with consistent allowance for the interaction of the vibrational and rotational motions of the molecule. In this case the intensities, half-widths, and positions of the line centers are all obtained theoretically, which makes possible an analysis of all lines of the spectrum.

2. The problem of the vibrational-rotational energy levels of molecules of the asymmetric-top type has been solved by a number of authors ($^{3-7}$). In (^{7}) it was shown that, in order to achieve a calculation accuracy satisfying the experimental data on molecular terms, when solving the Schrödinger equation by perturbation theory it is not sufficient to use the first and second approximations. The use of higher orders, however, proves difficult because of the cumbersome form of the expression for the energy operator ($^{3-5}$).

The energy operator used by us is obtained as follows. The classical vibrational-rotational Hamiltonian of polyatomic molecules is represented in the form

$$T(q,p,P) = T'(q,p,P) + Q(q)A(q,p), \tag{1}$$

where q are normal coordinates; p are the generalized momenta conjugate to q; P are the projections of the total angular momentum on the coordinate axes;

$$A = \left[\sum_{ik} G^z_{ik} q_i p_k \right]^2 .$$

In formula (1), $T'(q, p, P)$ is the principal part of the energy, for which the quantum-mechanical operator is obtained unambiguously by replacing the classical quantities by the corresponding operators; $Q(q)$ is a certain function of the normal coordinates. After expanding $Q(q)$ in a series in the normal coordinates and symmetrizing the products $q^n A(q,p)$ $(n = 0, 1, 2, ...)$, the writing of the operator presents no difficulty. The Hamiltonian obtained in this way is approximate; however, it retains all the qualitative features of the exact Hamiltonian. It contains the operators of rotational energy, vibrational energy, and an operator due to the interaction of vibrations and rotation, with the first and third of the listed operators having the same form as in the exact Darling–Dennison Hamiltonian (^{5}). The second term, although it differs from the exact one, differs only beginning with terms of the fifth degree in the expansion.

potential function in normal coordinates. At present there are no sufficiently reliable values of the fifth-order anharmonicity constants; therefore one may assert that the approximate Hamiltonian obtained in this way provides quite sufficient accuracy for practical calculations.

The Schrödinger equation can now be written in the form

$$\left[H_v + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} P_\alpha P_\beta - \frac{1}{2} P_z (\mu'_{zz} P_z + P_z \mu_{zz}) \right] \psi = E\psi, \qquad (2)$$

where H_v is the Hamiltonian of anharmonic vibrations; P_α is the projection of angular momentum on the α axis $(\alpha = x, y, z)$; $\mu_{\alpha\beta}$ is a certain function of the normal coordinates (the notation of Ref. (3) is used here).

As the zeroth approximation in solving (2) we take the problem of a three-dimensional anharmonic oscillator and a nonrigid asymmetric top. The energy operator of the latter, in the third order of perturbation theory, is obtained as follows:

$$H^{[v]}_{j\tau} = \frac{1}{2} \sum_{\alpha}^{xyz} a_{\alpha\alpha} P^2_\alpha + \frac{1}{4} \sum_{\alpha\beta\gamma\delta}^{xyz} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta + \frac{1}{8} \sum_{\alpha\beta\gamma\delta\varepsilon\eta}^{xyz} V_{\alpha\beta\gamma\delta\varepsilon\eta} P_\alpha P_\beta P_\gamma P_\delta P_\varepsilon P_\eta \qquad (3)$$

For the effective rotational constants $a_{\alpha\alpha}$ and the centrifugal-distortion constants τ and V, we have obtained analytical formulas that make it possible to represent the constants $a_{\alpha\alpha}$, τ, V as polynomials (of fourth degree in the case of $a_{\alpha\alpha}$, and of second degree in the case of τ and V) in the vibrational quantum numbers.

The operator $H_{j\tau}^{[v]}$ is introduced into (2) in the following way:

$$\left[H_v + H_{j\tau}^{[v]} + H_{RV} - H_{j\tau}^{[v]}\right]\psi = E\psi. \tag{4}$$

Here H_{RV} denotes the second and third terms on the left-hand side of (2). Solving equation (4) by the perturbation method, with the operator $H_v + H_{j\tau}^{[v]}$ as the zeroth-approximation operator, we find that, to within the terms omitted in (3), the total vibrational-rotational energy is represented, for the levels of greatest practical interest, in any order of perturbation theory in the form $Ev_{j\tau} = E_v + E_{j\tau}^{[v]}$, where E_v is the total vibrational energy with anharmonicity taken into account, and $E_{j\tau}^{[v]}$ is the eigenvalue of the operator $H_{j\tau}^{[v]}$.

The eigenfunctions of the complete vibrational-rotational Hamiltonian are found from (4) by the perturbation method. Thus, in the zeroth approximation,

$$\psi_{vj\tau} = \psi_v \psi_{j\tau}^{[v]}, \tag{5}$$

where ψ_v is the vibrational function with anharmonicity taken into account, normalized with the weight function (4), and $\psi_{j\tau}^{[v]}$ is the eigenfunction of the nonrigid top.

To calculate the line centers, the vibrational energy levels were taken from Ref. (8). The energies and wave functions of the nonrigid top were determined by diagonalizing the operator matrix in a basis of symmetric-top functions. For convenience of calculation, the operator $H_{j\tau}^{[v]}$ was transformed. The new expression contained only 21 coefficients. Their values were determined from experimental data by the method of least squares.

3. In calculating line intensities, the principal difficulty is the computation of the matrix element of the dipole moment. Expression (5) for the complete vibrational-rotational function makes it possible to represent the mat-

rotational element in the form of products of the matrix elements of the direction cosines by the matrix elements of the normal coordinates. In this case the vibrational function ψ_v is written in first-order perturbation theory, while the function $\psi_{j\tau}^{[v]}$ is represented as a series in generalized spherical functions $D_{mk}^{j}(\alpha,\beta,\gamma)$

$$\psi_{j\tau m}^{[v]} = \sum_k g_k^{[v]}(j\tau)\left(\frac{8\pi^2}{2j+1}\right)^{-1/2} D_{mk}^{j}(\alpha,\beta,\gamma). \tag{6}$$

Fig. 1. Spectral variation of the absorption coefficient of water vapor in the spectral interval 11890-11915 cm^{-1} for the near-ground layer of the atmosphere

Figure 1: Fig. 1. Spectral variation of the absorption coefficient of water vapor in the spectral interval 11890-11915 cm^{-1} for the near-ground layer of the atmosphere

Here α, β, γ are Euler angles. In calculating the coefficients $g_k^{[v]}(j\tau)$, the influence of centrifugal distortion on their magnitude is taken into account. The values of the coefficients for the upper and lower levels are different. In work (2) they are taken to be identical. The dipole moment of the molecule in the coordinate system rigidly bound to it was represented in the form

Fig. 1. Spectral variation of the absorption coefficient of water vapor in the spectral interval 11890-11915 cm^{-1} for the near-ground layer of the atmosphere

$$\mu = \mu^0 = \sum_i \mu^i q_i + \sum_{ik} \mu^{ik} q_{iq} k. \tag{7}$$

The coefficients μ^i, μ^{ik} were determined from experimental data on the absolute intensities of vibrational-rotational bands (2,9,10). In doing so, the matrix elements of the dipole-moment operator were calculated with allowance for the weight function (4).

4. Expressions (7) and (5) for the dipole moment and the complete vibrational-rotational function made it possible to apply, for the calculation of line half-widths, the basic scheme of Anderson’ s method (11,12), modifying it in such a way that it became possible to take into account the influence of vibrational anharmonicity and of the centrifugal-distortion effect.

In the calculations of line half-widths, nitrogen was considered as the broadening gas. Bearing in mind that the effective collision cross sections of water molecules with nitrogen molecules and with oxygen molecules differ little from one another (1), it may be assumed that the calculation results characterize the broadening of the lines due to collisions of H_2O molecules with air.

5. To find the positions of the line centers, their intensities, half-widths and, on their basis, the coefficients of monochromatic absorption, calculation programs were compiled for the M-20 electronic digital computer. With the aid of these programs, the calculation of the indicated quantities can be carried out for any region of the vibrational-rotational spectrum of water vapor.

For a number of narrow spectral intervals in the regions 0.84; 1.06; 1.15 μ, calculations of monochromatic absorption coefficients were performed with a step of 0.01—0.005 cm^{-1} for several pairs of pressure and temperature values.

Figure 1 gives an illustration of these calculations. For a spectral interval 25 cm^{-1} wide in the region 0.84 μ, the graph shows the spectral curve of the absorption coefficient k_ν for standard values of pressure and temperature at the Earth. It is evident from the figure that the absorption coefficient in the narrow spectral interval under consideration changes by 4 orders of magnitude. We note that, in calculating the attenuation of radiation in the atmosphere, absorption in this region is neglected in comparison with aerosol scattering ([1]). It is evident from the figure that this neglect is justified, since for

for most intervals of the spectrum $k_\nu < 10^{-2}$ cm^2/g. However, at the centers of individual lines $k_\nu > 1$. This means that, at average humidity, absorption in these cases will be substantially greater than aerosol scattering even in very dense haze. The conclusions drawn are valid not only for the conditions of the near-surface layer of the atmosphere, since the values of k_ν increase with altitude at the centers of the lines and decrease in the wings.

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Note: Figure translations are in progress. See original paper for figures.