THE WATER VAPOR DIMER AND ITS SPECTRUM

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Abstract

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THE WATER VAPOR DIMER AND ITS SPECTRUM

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To calculate the rotational spectrum of the water-vapor dimer we use a linear model of the dimer, the structure of which was considered in ([1], p. 415). This is a compound with internal rotation: one water molecule undergoes hindered rotation relative to the other molecule about the line of the hydrogen bond O ··· O_2 in the potential field $V(\alpha) = \frac{1}{2}V_0(1-\cos\alpha)$, where α is the relative angle of rotation of the molecules about the bond line; V_0 is the height of the potential barrier, equal to 455 cm^{-1} (1.3 kcal/mole).

Burkhard and Irwin ([2]), using the method of internal axes ([3-5]), considered the general case of two asymmetric tops undergoing hindered rotation relative to one another (the water-vapor dimer is precisely such a compound). The Hamiltonian can be represented as the sum of three terms $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3$, where $\hat{H}_1$ is the Hamiltonian of an effective symmetric top, which describes the rotation of both groups forming the dimer, or the "external" rotation; the operator $\hat{H}_2$ describes the "internal," or hindered, rotation in the potential field $V(\alpha)$; the operator $\hat{H}_3$, due to the asymmetry of the compound, describes the interaction of the "external" and "internal" rotations.

We calculate the matrix elements of the Hamiltonian with the aid of the basis eigenwave functions of the operator $\hat{H}_0 = \hat{H}_1 + \hat{H}_2$, equal to

$$U_{JKMv} = \frac{1}{2\pi} e^{iK\varphi} e^{iM\psi} \Theta_{JKM}(\theta) P_{vK}(\alpha) \exp\left[-i\frac{C_1}{(C_1+C_2)}K\alpha\right]. \qquad (1)$$

Here θ, φ, ψ are the Euler angles; moreover

$$\varphi = \frac{C_1}{(C_1+C_2)}\varphi_1 + \frac{C_2}{(C_1+C_2)}\varphi_2,$$

where φ_1 and φ_2 are the angles of rotation, respectively, of the first and second water molecules about the internal-rotation axis; C_1 and C_2 are the moments of inertia about this axis for the first and second water molecules. The factor

$e^{iK\varphi}e^{iM\psi}\Theta_{JKM}(\theta)$ in formula (1) is the usual wave function of a symmetric top (J is the quantum number of the total angular momentum; K and M are the quantum numbers of the projections of the angular momentum, respectively, on the internal-rotation axis and on an axis fixed in space). The factor $F_{vK}(\alpha) = P_{vK}(\alpha)\exp\left[-i\frac{C_1}{(C_1+C_2)}K\alpha\right]$ is the wave function for internal rotation, satisfying the equation for a hindered rotor ([6]); v is the torsional quantum number.

The matrix elements of the interaction operator $\hat{H}_3$ in this representation are small and we shall not take them into account. The eigenvalues of the operator $\hat{H}_0$ are equal to the sum of two terms. The first term, describing the "external" rotation, is the rotational energy of an effective symmetric top and is given by the expression

$$E_{JK} = \frac{\hbar^2}{2}\left\{\frac{1}{4N'}\left[C_1C_2(A_1+A_2+B_1+B_2) - C_1E_2^2 - C_2E_1^2\right](J^2+J-K^2) + \frac{K^2}{C}\right\},$$

where $A_1, A_2, B_1, B_2, C_1, C_2, C, E_1, E_2$ are moments and products of inertia, defined in (2); N' is a function of these quantities (see ibid.); h is Planck' s constant.

The data on the dimer configuration needed for estimating these constants were taken from ([1a]). We also note that, in calculating E_{JK}, the displacement of the dimer center of inertia relative to the axis of internal rotation was neglected because of its smallness. As a result, taking into account the parameters of the H_2O dimer, the energy E_{JK} can be written in the form

$$E_{JK} = 0.23J(J+1) + 7.07K^2 \ \ (\mathrm{cm}^{-1}).$$

The second term, E_{vK}, characterizing the energy of internal rotation, is equal to ([6])

$$E_{vK} = \frac{4V_0}{s}\sum_{l=0}^{\infty} a_l \cos\left[2\pi\frac{C_1}{(C_1+C_2)}Kl\right].$$

Here the coefficients a_l depend on the torsional quantum number v and the reduced barrier height s (see ([6,7])); for the dimer $s = 60$. Using the tables of Ref. ([8]), the values of E_{vK} were found for $s = 60$ and $v = 0, 1, 2$:

$$E_{0K} = 58.2 \ \ (\mathrm{cm}^{-1}), \qquad E_{1K} = 170.3 \ \ (\mathrm{cm}^{-1}),$$

$$E_{2K} = \left\{272.9 - 0.1477\cos\left[2\pi\frac{C_1}{(C_1+C_2)}K\right]\right\} \ \ (\mathrm{cm}^{-1}). \qquad (2)$$

As is evident, the Fourier series in the expression for E_{vK} converges very rapidly, and E_{vK} depends only weakly on K. This is true when the barrier to internal rotation is sufficiently high. The barrier belongs to the category of "high" barriers if $s \geq 20$ (or $V_0 \geq 0.7$ kcal/mol ([6])). In this case (which also applies to the dimer), internal rotation may be considered in the harmonic-oscillator approximation for energies E_{vK} not exceeding the barrier height. For the H_2O dimer, the number of molecules with energy $E_{vK} \geq V_0$ constitutes no more than 5% of the total number of dimers.

In the harmonic-oscillator approximation, the energy of internal rotation reduces to the energy of torsional vibrations $E_v = 200(v + 1/2)$ (cm^{-1}). It is seen that this approximation agrees fairly well with the exact solution for $v \leq 2$ (see the values (2) given above). It is difficult to make an equally definite statement about the energies with quantum number $v > 2$, owing to the absence of tables for a_l at $v > 2$. In what follows, when considering internal rotation, we shall approximate the exact wave functions $F_{vK}(\alpha)$ by the harmonic-oscillator wave functions $\mathcal{H}_v(\alpha)$, and take the values (2) as the energies.

The absorption coefficient γ can be calculated from formula ([7])

$$\gamma \left[\frac{\partial \delta}{KM}\right] = 10^6 \log_{10} e \, \frac{32\pi^2 N}{3hcG(T)\lambda^2} \sum_{ij} |\mu_{ij}|^2 \, \frac{1}{\lambda_{ij}} \times$$

$$\times \left|e^{-E_i/kT} - e^{-E_j/kT}\right| \frac{(\Delta\nu/c)^0_{ij}\sqrt{T/293}\,(P/760)}{\left[(1/\lambda_{ij})^2 - (1/\lambda)^2\right]^2 + 4\left[(\Delta\nu/c)^0_{ij}\sqrt{T/293}\,(P/760)\right]^2 (1/\lambda)^2}. \tag{3}$$

Here i and j denote the set of quantum numbers corresponding to nondegenerate rotational quantum states; the summation is carried out over all quantum transitions; λ is the wavelength of the electromagnetic radiation; λ_{ij} is the resonance wavelength of the dimer molecule for the transition from state i to state j; E_i and E_j are the energies of the i- and j-states, respectively; $(\Delta\nu/c)^0_{ij}$ is the half-width of the spectral line in cm^{-1} at absolute temperature $T = 293^\circ$ and pressure $P = 760$ mm Hg for the transition $i \to j$; the factor $\sqrt{T/293}$ determines the temperature dependence of the half-widths of the spectral lines of the dimer under the assumption that the effective collision cross section of the dimer with surrounding molecules does not depend on their relative velocity; h, c, and k are, respectively, the constants

Planck' s constant, the speed of light, and Boltzmann' s constant; $G(T)$ is the statistical sum, equal to

$$G(T) = \sum_{JKv} g_I(2J+1) \exp\left[-\frac{(E_{JK} + E_{vK})}{kT}\right],$$

where g_I is the nuclear statistical weight. For a random symmetric top (which the H_2O dimer is), nuclear spin increases the statistical weight by the same factor for all rotational levels, as a result of which the factor g_I does not enter into the expression for the absorption coefficient. If inversion doubling is also not taken into account, then the statistical weight of levels with $K = 0$ will be equal to $(2J + 1)$, and the statistical weight of levels with $K \neq 0$ will be $2(2J + 1)$. In the expression for γ the form of the spectral line obtained from the solution of the kinetic equation ([9,10]) was used. The quantity N in (2), $N = 10^{-6}\rho_d N_0/\eta$, is the number of water-vapor dimer molecules in 1 cm^3. Here $N_0 = 6.025 \cdot 10^{23}$ is Avogadro' s number; $\eta = 36$ is the molecular weight of the dimer; ρ_d is the concentration of dimers (in g/m^3). In calculating γ, the quantity ρ_d was computed for a hydrogen-bond energy equal to 5.2 kcal/mol ([11]), at an absolute air humidity $\rho_{H_2O} = 7.5$ g/m^3, and at $T = 293^\circ$. As a result, from formulas ((16), p. 424) we obtain $\rho_d = 0.022$ g/m^3, i.e., the number of dimers in the atmosphere is about 0.1% of the number of water-vapor monomers. The quantity $|\mu_{ij}|^2$ in the expression for γ is the square of the modulus of the matrix element of the dipole moment for the transition $i \to j$. The water-vapor dimer possesses a component of the electric dipole moment not only in the direction of the symmetry axis of the effective symmetric top (the axis of internal rotation), but also in the direction perpendicular to it, since the top is a random symmetric rotor and not due to the symmetry of the compound.

Because the basis wave function $U_{JKMv}(\alpha)$ is equal to the product of functions describing, respectively, the symmetric top (a function of the Euler angles) and the hindered rotor ($F_{vK}(\alpha)$), the quantity $|\mu_{ij}|^2$ can be written in the form

$$|\mu_{ij}|^2 = \frac{\beta_{ij}}{(2J+1)} \left\{ \langle F_{v_{iK}i}(\alpha)|\mu|F_{v_{jK}j}(\alpha)\rangle \right\}^2,$$

where the quantum number J refers to the i-th state, $\langle F_{v_{iK}i}(\alpha)|\mu|F_{v_{jK}j}(\alpha)\rangle$ is the matrix element of the modulus of the electric moment causing the transition $i \to j$, obtained with the aid of the wave functions of internal rotation $F_{vK}(\alpha)$; β_{ij} is the oscillator strength of the quantum transition $J_i,\ K_i \to J_i,\ K_J$ for a rigid symmetric top (the values of β_{ij} for $J,\ K < 12$, obtained from rigorous formulas, were taken from tables ([12]); for quantum numbers $J,\ K \geq 12$, the quantities β_{ij} were calculated by us from tables ([12]) by means of finite-difference calculation).

The selection rules for radiative transitions between the energy levels of a symmetric top with hindered internal rotation for the component of the electric dipole moment lying along the axis of internal rotation are: $\Delta J = \pm 1;\ \Delta K = 0;\ \Delta v = 0$. In this case the quantity $\left\{ \langle F_{v_{iK}i}(\alpha)|\mu_\parallel|F_{v_{iK}i}(\alpha)\rangle \right\}^2 = |\mu_\parallel|^2 = 4.1774 \cdot 10^{-36}$ $(CGSE)^2$. Using the constants of the H_2O dimer, one may say that these transitions give a series of lines $(\nu/c)_{ij} = 0.46\,J$ (cm^{-1}), characteristic of symmetric rotors.

For the component of the dipole moment perpendicular to the axis of internal rotation, the selection rules are: $\Delta J = \pm 1,\ 0;\ \Delta K = \pm 1$; the quantity Δv is indeterminate. However, for high potential barriers (more precisely, for levels $E_{vK} < V_0$, when the harmonic-oscillator approximation is valid), internal rotation is close to torsional vibrations and $\Delta v = \pm 1,\ 0$.

Consider the transition $J, K, v \to J', K-1, v'$. Using the expressions for the energies E_{JK} and E_{vK}, and taking into account that $J \geq K$, the frequencies of such transitions can be written as follows (in cm^{-1}):

$$(\nu/c)_{J\to J-1} = \nu'/c + 0.46J; \qquad J = K,\ K+1,\ K+2, \ldots \qquad (P\text{-branch}),$$

$$(\nu/c)_{J\to J} = \nu'/c \qquad (Q\text{-branch}),$$

$$(\nu/c)_{J\to J+1} = \nu'/c - 0.46J; \qquad J = K+1,\ K+2, \ldots \qquad (R\text{-branch}),$$

where

$$\nu'/c = 7.07(2K-1) + (E_{vK} - E_{v'K-1})/hc.$$

Transitions for which $K-1 \to K$ will have the same structure. Let us note that in the P- and R-branches the distance between the lines corresponding to one and the same value of v is constant and, for the H_2O dimer, is equal to 0.46 cm^{-1}; the lines of the Q-branch (which are the most intense) for one and the same value of v are separated from one another by 14.14 cm^{-1}. Each of the Q-branch lines in fact consists of a large number of individual "sublines," corresponding to different values of the quantum number J (which, for small K, can take large values up to $J = 70$).

In what follows we shall be interested in transitions with $\Delta v = 0$. They correspond to the purely rotational spectrum of the symmetric top. Neglecting the interaction of rotation with torsional vibrations (as well as with other vibrations), we obtain for transitions $\Delta K = \pm 1$ and $\Delta v = 0$ that the quantity

$$\{\langle F_{viK_i}(\alpha)|\mu_\perp|F_{viK_j}(\alpha)\rangle\}^2 \simeq \{\langle \mathcal{H}_{vi}(\alpha)|\mu_\perp|\mathcal{H}_{vi}(\alpha)\rangle\}^2.$$

For the value of this quantity averaged over torsional states with energies $E_v < V_0$, we obtain $6.5 \cdot 10^{-36}$ $(\text{CGSE})^2$. In calculating the matrix elements of the dipole moment of the dimer, the dipole moment of the H_2O monomer was taken to be $1.8 \cdot 10^{-18}$ CGSE.

Transitions with $\Delta v = \pm 1$ will correspond to the rotational-vibrational spectrum of the dimer. They lie in the region $(\nu/c)_{ij} \sim 100$ cm^{-1} and require special consideration. Transitions with $\Delta v > 1$ lie in the region $(\nu/c)_{ij} > 100$ cm^{-1} and are less intense.

For energies $E_{vK} > V_0$ (which is realized for approximately 5% of the H_2O dimers), the internal rotation may be regarded as free. It can be shown that such molecules contribute to the absorption only for $(\nu/c) > 90$ cm^{-1}.

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