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# Temperature dependence of the intensity of the vibration-rotational absorption band $\nu_2$ of $H_2O$ trapped in an argon matrix

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ABSTRACT

Using two sets of effective rotational constants for the ground (000) and the excited bending (010) vibrational states the calculation of frequencies and intensities of vibration-rotational transitions for $J''=0-2$; and $J'=0-3$; was carried out in frame of the model of a rigid asymmetric top for temperatures from 0 to 40 K. The calculation of the intensities of vibration-rotational absorption bands of $H_2O$ in an Ar matrix was carried out both for thermodynamic equilibrium and for the case of non-equilibrium population of para- and ortho-states. For the analysis of possible interaction of vibration-rotational and translational motions of a water molecule in an Ar matrix by 3D Schrödinger equation solving using discrete variable representation (DVR) method, calculations of translational frequencies of $H_2O$ in a cage formed after one argon atom deleting were carried out. The results of theoretical calculations were compared to experimental data taken from literature.

## 1. Introduction

Water molecule is the object of numerous investigations due to its essential biological, chemical and ecological properties [1–4]. Great attention has been paid to the analysis of vibration-rotational spectra of water in the gas phase [5–8]. Considerable progress has been made in improving the accuracy of theoretical methods to compute potential energy surfaces and dipole moments which has allowed impressive success in the prediction of frequency and intensity values of vibration-rotational transitions of a water molecule up to 30,000 $cm^{-1}$ [9–13]. Being an asymmetric top with two equivalent spin 1/2 nuclei, the $H_2O$ molecule can exist in para- and ortho-spin states. In the first case, the spins of the protons are singlet coupled with total spin zero, while in the second case they are triplet coupled with spin quantum number equal to 1. In the absence of magnetic fields the ortho-state is three-fold degenerate through the magnetic spin quantum number, while the para-state is always non-degenerate. The requirement of antisymmetry of the total wave function under permutations of identical nuclei requires taking into account the symmetry of vibrational and rotational wave functions in combination with the nuclear spin wave functions. The latter are symmetrical for ortho-states in relation to exchanging the hydrogen atoms and antisymmetrical for para-states which becomes of importance when considering the rotational states of the molecule. The symmetry of rotational wave functions in terms of permutations of identical nuclei can be determined from the values of the rotational quantum numbers. For highly symmetrical molecules of asymmetric top type (to which the $H_2O$ molecule belongs) vibration-rotational transitions are divided into a, b and c types with dependence on the main axis of inertia $a$, $b$ or $c$ (main inertia moments are denoted increasingly as $I_a \prec I_b \prec I_c$), along which the transition dipole vector is directed. Thus, it is clear that vibration-rotational transitions when totally symmetrical vibrations are excited belong to $b$ type, since the change of the dipole moment vector for these vibrations is directed along the bisectrix of the H—O—H angle, coinciding with the main axis of the middle moment of inertia, and those when antisymmetric vibrations are excited – to $a$ type. The main axis corresponding to the largest moment of inertia is normal to the molecule plane and, since the dipole moment vector is always in the molecular plane, it is obvious that bands of $c$ type in the case of $H_2O$ cannot be realized.

Matrix isolation methods are very useful for investigating individual molecules and their clusters [14–19]. It is believed [20–26] that due to its small size the molecule of water can be in the excited rotational and vibration-rotational states in an isolating matrix in the case of small values of rotational quantum numbers $J''$ and $J'$. The state of the molecule, which can be considered as an asymmetric top with some

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effective values of the rotational constants ($A_{v_1v_2v_3}, B_{v_1v_2v_3}, C_{v_1v_2v_3}$), can be described by the following set of quantum numbers ($v_1v_2v_3, J_{k_ak_c}$), where $v_1, v_2, v_3$ are vibrational quantum numbers characterizing symmetric stretching, bending and asymmetric stretching vibrations of O—H bonds, respectively, and $J_{k_ak_c}$ - the standard set of quantum numbers describing the rotational state of an asymmetric top [27,28]. Symmetry or antisymmetry of rotational wave functions relative to permutation of hydrogen atoms is determined by the parity of the sum of quantum numbers $k_a + k_c$. Taking into consideration the symmetry properties of the wave functions mentioned above, it is clear that in the ground and excited bending vibrational states the para-state is realized in the case $k_a + k_c = even$, and the ortho-state – in the case $k_a + k_c = odd$. Rotation leads to a more complicated observed IR spectrum, in spite of low temperatures ($T < 40$ K). At the same time, this fact allows observing fine effects of interaction of a rotating $H_2O$ molecule with a matrix and possibly as well with translational vibrations of a molecule as a whole in a cage. The first serious analysis of rotational and vibration-rotational states of a water molecule in an argon matrix was made by Perchard [24]. Based merely on rotational and vibration-rotational spectra and using the theoretical model of Manz [29] and some assumptions on an inertial defect ($\Delta = I_C - I_A - I_B$) of $H_2O$ in gas phase and in a matrix, he managed to obtain a set of vibrational constants of water monomer in the ground and excited states in an Ar matrix. An assignment of the observed absorption bands to specific vibration-rotational transitions was proposed taking into account overtones and combination bands. Later [25] some assignments in [24] were questioned. In particular, the bands near 1660 cm$^{-1}$ were reassigned to be related to interaction of rotational and translational motions. In [26] the same authors have obtained alternative sets of rotational constants in the ground and excited vibrational states based on the analysis of intensities of absorption bands, which were due to the transitions from the lowest levels for para - ($000,0_{00}$) and ortho- ($000,0_{01}$) states. Using well-known formulae [27,28] the authors of [26] have calculated energies of vibration-rotational levels for $J'', J' \leq 2$; and obtained frequency values of transitions, some of which differed from experiment, but not by more than 18 cm$^{-1}$. An analysis of redistribution of intensities of vibration-rotational bands with changing temperature in [25,26] was made based on data on vibration-rotational spectra of water in gas phase in thermodynamic equilibrium.

In later investigations [30–34] the authors focused on the analysis of intercombinatory transitions in water monomer in matrix isolation. It is obvious that calculations of intensities of individual components of rotational structure for the bending vibration in $H_2O$ molecule at different temperatures taking into account effective values of rotational constants from [24,26] both at thermodynamic equilibrium and without it (which is typical for the spectra registered immediately after deposition of water molecules and Ar atoms onto a window) is an interesting and important task, which can confirm or refine the proposed assignments of absorption bands. An analysis of the possibility of interaction between vibration-rotational and translational motions of a water molecule in an Ar matrix requires an independent estimation of translation vibrational frequencies. These problems are considered in the present work.

## 2. Determination of the energy of rotational states and intensities of vibration-rotational transitions

According to [35,36] the intensity of a vibration-rotational transition can be calculated by the formula:

$$I_{i\to f} = \frac{(2\pi)^3 N\tilde{\nu}_{if} g_{s(i)} \left[e^{-\frac{E_i}{kT}} - e^{-\frac{E_f}{kT}}\right]}{4\pi\varepsilon_0 3hcQ(T)} \left(3\langle\Psi_{vi}\Psi_{ri}|\mu_Z|\Psi_{vf}\Psi_{rf}\rangle\right)^2 \tag{1}$$

where $i, f$ denote initial and final state, $N$ - the concentration of the studied molecules, $\tilde{\nu}_{if}$ - the wavenumber of the transition, $g_{s(i)}$ - the spin degeneracy order of the initial state, $E_i, E_f$ - the initial and final state energies, $Q(T)$ - the partition function over states, $\Psi_{vi}, \Psi_{ri}, \Psi_{vf}, \Psi_{rf}$ - vibrational and rotational functions in initial and final states, $\mu_Z$ - $Z$-th component of the dipole operator in the laboratory-fixed coordinate frame with origin at the center of mass of the molecule. According to the symmetry of the $H_2O$ molecule, we select as $z$ axis of the molecule-fixed coordinate frame the $C_2$ rotational axis of symmetry, and the $y$ axis located in the plane of the molecule (Fig. 1).

In the expression (1) the exponent with energy in the final state at temperatures below 50 K can be neglected. The wave function of an asymmetric top ($J_{k_ak_c}$) can be presented as a linear combination of wave functions of a symmetric top [27,28,37,38]:

$$J_{k_ak_c} = \sum_{K=-J,1,J} C_K^{J_{k_ak_c}} |JKM\rangle. \tag{2}$$

Since only relative intensities of fine-structure components of the vibrational band $\nu_2$ are interesting for us, then taking into account Eq. (2) and according to [36,38–40] we rewrite Eq. (1) as follows:

$$I_{i\to f} = \frac{Const \cdot N\tilde{\nu}_{if} g_{s(i)} e^{-\frac{E_i}{kT}}}{Q(T)} \left(2J'' + 1\right) \times (2J' + 1) \left[\sum_{K=-Min\{J'',J'\},1,Min\{J'',J'\}} C_K^{J''_{k''_ak''_c}} \cdot C_K^{J'_{k'_ak'_c}} \cdot \begin{pmatrix} J'' & 1 & J' \\ K & 0 & -K \end{pmatrix}\right]^2. \tag{3}$$

In the case of an equilibrium population of levels, $N$ is constant and can also be included in $Const$. Energies of rotational states and coefficients $C_K^{J'_{k'_ak'_c}}$ are determined by diagonalization of a Hamiltonian matrix, which has the following tridiagonal structure ($J = 3$):

$$\begin{pmatrix} d_3 & 0 & a_2 & 0 & 0 & 0 & 0 \\ 0 & d_2 & 0 & a_1 & 0 & 0 & 0 \\ a_2 & 0 & d_1 & 0 & a_0 & 0 & 0 \\ 0 & a_1 & 0 & d_0 & 0 & a_1 & 0 \\ 0 & 0 & a_0 & 0 & d_1 & 0 & a_2 \\ 0 & 0 & 0 & a_1 & 0 & d_2 & 0 \\ 0 & 0 & 0 & 0 & a_2 & 0 & d_3 \end{pmatrix}. \tag{4}$$

The diagonal elements are given by the formula:

$$\langle JKM|CJ_c^2 + AJ_a^2 + BJ_b^2|JKM\rangle = \frac{A+C}{2}\left[J(J+1) - K^2\right] + BK^2; \tag{5}$$

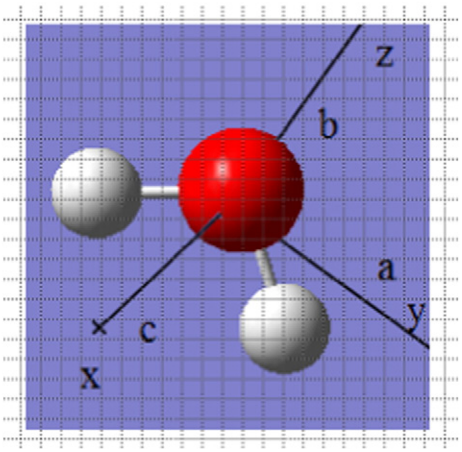

**Fig. 1.** Definition of the molecule-fixed coordinate frame.