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Vibrational Frequencies of Water Isotopologues : Vibron Model

Research Article

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Abstract: In this paper, calculated vibrational frequencies of water isotopologues, Deuterium oxide (D_2O), Water-^{18}O ($H_2{}^{18}O$) in fundamental level using Hamiltonian expression, which is in terms of invariant and Majorana operators describe stretching vibrations.

Keywords: Vibrational spectra, Water Isotopologues, Vibron Model.

1. Introduction

In 1981, Iachello introduced Vibron model for the calculation of vibrational spectra of molecules [1]. The study of vibrational spectra is essential to understand both experimental and theoretical approaches. There are two traditional methods (Dunham expansion and Potential approach) to explain molecular vibrations. The main drawback of these approaches is that more complex to fit parameters if the numbers of atoms are increase in molecule. To overcome the difficulty to analyze the vibrational spectra of molecules by traditional methods, we consider the Vibron model [2–4].

2. Lie Algebraic Method (Triatomic Molecule)

The Hamiltonian (molecular vibrations) for polyatomic molecules is of the form

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij} \tag{1}$$

Here i change from 1 to n for n stretching bonds and A_i, A_{ij} and λ_{ij} are algebraic parameters, which are determined by spectroscopic data. Where C_i (uncoupled bonds) is an invariant operator with eigenvalues $-4\left(N_i v_i - v_i^2\right)$ and the operator C_{ij} (coupled bonds) with diagonal matrix elements

$$\langle N_i, v_i; N_j, v_j \left| C_{ij} \right| N_i, v_i; N_j, v_j \rangle = 4\left[(v_i + v_j)^2 - (v_i + v_j)\left(N_i + N_j\right)\right],$$

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while the Majorana operator M_{ij} has both diagonal and non-diagonal matrix elements

$$\langle N_i, v_i; N_j, v_j \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle = (N_i v_j + N_j v_i - 2v_i v_j)$$
$$\langle N_i, v_i+1; N_j, v_j-1 \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle = -[v_j\,(v_i+1)\,(N_i - v_i)\,(N_j - v_j + 1)]^{1/2}$$
$$\langle N_i, v_i-1; N_j, v_j+1 \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle = -[v_i\,(v_j+1)\,(N_j - v_j)\,(N_i - v_i + 1)]^{1/2}.$$

v_i $(i = 1, 2, 3, \dots)$ represents vibrational quantum numbers. The vibron number N_i $(i = 1, 2, 3, \dots)$ for stretching bonds of molecule will be calculated from the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1,\ i = 1, 2, \dots \tag{2}$$

Here ω_e and $\omega_e x_e$ are the spectroscopic constants [5]. The initial guess value for the parameter A_i will obtain by the energy equation for the single-oscillator fundamental mode, which is given as,

$$E\,(v = 1) = -4A_i\,(N_i - 1) \tag{3}$$

Initial guess for A_{ij}may be taken as zero. The parameter λ_{ij}will obtain from the relation

$$\lambda_{ij} = \frac{|E_i - E_j|}{3N} \tag{4}$$

To obtain better results least squares fitting procedure is used for the parameters A_i, λ_{ij} starting from values as given by equations (3) and (4).

3. Results

Symmetry species, (C_{2v}) Point group	Vibrational frequencies			
	Experimental [6]		Calculated	
	D_2O	$H_2{}^{18}O$	D_2O	$H_2{}^{18}O$
A1 (sym. str.)	2671.46	3649.68	2673.34	3642.34
A1 (bend)	1178.33	1588.27	1177.92	1589.23
B1(anti str.)	2788.05	3741.58	2788.47	3742.02

Table 1. **Vibrational frequencies (cm^{-1})**

Parameters	D_2O	$H_2{}^{18}O$
N (str.)	50	44
N (bend)	19	28
A_i (str.)	-13.92	-18.92
A_i(bend)	-12.22	-14.23
A_{ij} (str.)	-0.142	-1.11
A_{ij}(bend)	-1.323	-3.59
λ_{ij} (str.)	0.77	1.08
λ_{ij}(bend)	0.82	1.63

Table 2. **Fitting parameters**

4. Conclusions

In this paper we have calculated vibrational frequencies of Deuterium oxide, Water-^{18}O in fundamental level using Vibron model. The obtained results are in good agreement with the experimental values.

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