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MP4 study of the multimode coupling in protonated water dimer

G. Pitsevich [a, *], A. Malevich [a], E. Kozlovskaya [a], E. Shalamberidze [a], I. Doroshenko [b], V. Pogorelov [b], E. Mahnach [a], V. Sapeshko [c], V. Balevicius [d]

[a] Department of Physical Optics, Belarusian State University, Nezavisimosti Ave., 4, 220030 Minsk, Belarus
[b] Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64|13, 01601 Kyiv, Ukraine
[c] University of Illinois at Chicago, Chicago, USA
[d] Faculty of Physics, Vilnius University, Sauletekio Al. 9-3, LT-10222 Vilnius, Lithuania

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ABSTRACT

The structure and frequencies of the protonated water dimer normal vibrations were calculated at the MP4/Aug-cc-pVTZ level of theory. Shared proton stretching vibrations were analyzed by constructing 4D potential energy surface using normal coordinates Q_6, Q_7, Q_8, Q_9, which describe intermolecular vibration of water monomers, stretching and bending vibrations of the shared proton, respectively. 1–4 dimensional vibrational Schrödinger equations were solved using the discrete variable representation method. Values of some anharmonic constants, responsible for the triple and quadruple modes coupling with the shared proton stretching vibrations were obtained. The efficiency of the hybrid method in the determination of the frequency of shared proton stretching vibrations was demonstrated during the solution of the vibrational problem with nD reduced dimension for all used values of n (n = 1–4).

1. Introduction

Modern quantum-chemical methods, that account the exchange effects and electron correlation, and employ sufficiently complete basis set, can quite accurately predict the vibrational frequencies of the majority of organic molecules in the frame of the harmonic approximation. However, anharmonicity effects of the vibrations can't be neglected for some molecules and molecular complexes. The most precise approach to this situation is to construct a 3N-6 dimensional potential energy surface ((3N-6) D PES), where N is the number of atoms in the molecule or complex. Then this multidimensional PES data is used to construct the Hamiltonian in corresponding multidimensional Schrödinger equation, and the kinetic energy operator is also presented in the most precise form. However, in general, this method requires a huge number of energy calculations. Indeed, for the completeness of description, energies for each vibrational coordinates are required to be found at least ten points, and the total number of energy calculations can generally be equal to 10^{3N-6}. However, if only one of the vibrational modes is anharmonic or investigation is focused on just one mode, then one usually solves a vibrational problem of the reduced dimensionality $n < 3N - 6$ by constructing nD PES, where, among the n coordinates, there is the specific one that describes the analyzed mode [1–5]. The accuracy of this approach can be improved by using a hybrid method [6–8], where the anharmonic interaction of the analyzed modes with other $3N - 6 - n$ modes, which do not participate in the construction of nD PES, is considered either through the anharmonic constants matrix, calculated in the frame of the standard model of anharmonicity accounting [9–11], or by using the "effective" anharmonic constants matrix, obtained after the solution of $3N - 6 - n$ 2D vibrational problems [12]. First, one can solve the one-dimensional vibrational problem (1D) by only varying the value of the analyzed coordinate in order to take into account the intrinsic anharmonicity. In the next approximation, the effect of the double anharmonic couplings with other modes on the analyzed mode can be taken into account by solving 3N-7 two-dimensional vibrational problems (2D). The more accurate value of the analyzed vibrational frequency can be obtained by solving $C^2_{3N-7} = \frac{(3N-7)(3N-8)}{2}$ three-dimensional vibrational problems (3D) and by calculating the corrections for triple anharmonic coupling with the other modes.

If the coupling between modes in the molecule is not significant, one can obtain quite accurate frequency value of the analyzed vibration by only taking into account its intrinsic anharmonicity.

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[*] Corresponding author.
E-mail address: pitsevich@bsu.by (G. Pitsevich).

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However, protonated water dimer (PWD), of course, belongs to a different category. The very first calculations of the shared proton stretching vibrations frequency (ν_7), performed using 2D PES construction [13], have indicated that the anharmonic coupling of this vibration with the symmetric intermolecular vibration of the water monomers leads to the frequency red shift of nearly 350 cm^{-1}. Then, in a papers series [14,15], the significant anharmonic coupling of the ν_7 with the two bending modes of the shared proton was mentioned. Recently, a significant anharmonic coupling of the ν_7 with antisymmetric bending vibrations of water monomers was noted [16]. In a forthcoming paper [12], we have analyzed in detail the double anharmonic couplings of ν_7 with all other PWD modes. This allowed us to establish that only a few modes have no effect on the ν_7 frequency. Such large influence of the mode coupling on the ν_7 frequency is one of the main reasons that, despite the long history of theoretical analysis of the shared proton vibrations dynamics [14,15,17–22], only recently the results, that are in the excellent agreement with the experimental data, were obtained [23–27]. However, at the moment it is still unknown whether triple coupling of modes or anharmonic coupling of a higher order can have any significant impact on the ν_7 frequency.

In the present paper calculation of the 4D PES was performed using the normal coordinates, which describe basic vibrational modes of the shared proton and intermolecular vibrations of the water monomers. Contributions of the three- and four-mode anharmonic coupling in the ν_7 frequency value were calculated. Also, it was shown that the three-mode couplings have a significant effect on the dynamics of the shared proton vibrations.

2. Calculations

Equilibrium configuration and IR spectra of the PWD were calculated in MP4 approximation [28] using Aug-cc-pVTZ basis set [29] without restrictions on the symmetry and with C_2 symmetry restriction using the quantum chemical package GAUSSIAN 09 [30]. Geometric structure parameters and spectral characteristics have coincided fully. Harmonic vibrational frequency values for C_1 and C_2 configurations are shown in Table 1. Calculated equilibrium C_2 configuration of the PWD is presented in Fig. 1.

Normal coordinates Q_6, Q_7, Q_8 and Q_9, which describe the intermolecular vibration of water monomers, stretching and bending vibrations of the shared proton respectively, were used for 4D PES construction. Normal coordinate's values were varied in the range $-0,6 \le Q_6, Q_7, Q_8, Q_9 \le 0,6$ with a step 0.1. The energy values at the nodes of the four-dimensional parallelepiped were calculated at MP4/Aug-cc-pVTZ level of theory. The 2D PES for Q_6 and Q_7 coordinates is shown in Fig. 2.

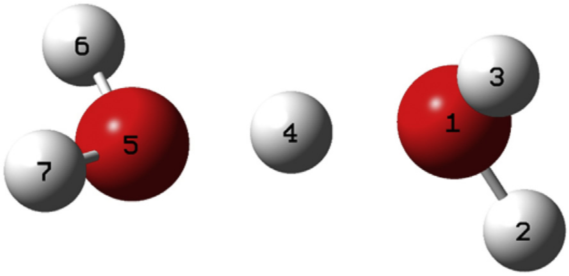

Fig. 1. Equilibrium geometry of PWD C_2 configuration with atoms numbering.

In order to find the position of the vibrational levels, the following Schrödinger equation was solved:

$$-\sum_{i=6}^{9} \frac{\hbar^2}{2\mu_{Q_i} l_0^2} \frac{\partial^2 \Psi}{\partial q_i^2} + U(q_6, q_7, q_8, q_9)\Psi = E\Psi \tag{1}$$

where $q_i = \frac{Q_i}{l_0}$; $l_0 = 1\text{Å}$; $\mu_{Q_i}-$ the reduced mass of $i-$th normal mode. Let us rewrite (1):

$$-\sum_{i=6}^{9} f_{q_i} \frac{\partial^2 \Psi}{\partial q_i^2} + U(q_6, q_7, q_8, q_9)\Psi = E\Psi; \quad f_{q_i} = \frac{\hbar^2}{2\mu_{Q_i} l_0^2}; \tag{2}$$

Equation (2) was solved numerically using the DVR method [31–34]. Hamiltonian matrix elements were calculated using formula [35,36]:

$$\begin{aligned} H_{(i,j,k,l),(i',j',k',l')} = {} & D_{ii'}^{q_6 q_6} \delta_{jj'} \delta_{kk'} \delta_{ll'} + \delta_{ii'} D_{jj'}^{q_7 q_7} \delta_{kk'} \delta_{ll'} + \delta_{ii'} \delta_{jj'} D_{kk'}^{q_8 q_8} \delta_{ll'} \\ & + \delta_{ii'} \delta_{jj'} \delta_{kk'} D_{ll'}^{q_9 q_9} \\ & + \delta_{ii'} \delta_{jj'} \delta_{kk'} \delta_{ll'} U\left(q_6^i, q_7^j, q_8^k, q_9^l\right); \end{aligned} \tag{3}$$

where $D^{qq} = (D^q)^T F^q D^q$; $F^q = f_q E^q$; $q \in \{q_6, q_7, q_8, q_9\}$ E^q - unit matrix, with a dimension corresponding to the dimension of the D^q matrix. In turn:

$$\begin{aligned} & D_{i'i}^q = \frac{(-1)^{i'-i}\omega_q}{2\sin\left[\frac{\pi(i'-i)}{2N_q+1}\right]}; \quad q \in \{q_6, q_7, q_8, q_9\}; \quad i', i \in \{1, 2, \ldots, 2N_q+1\}; \\ & D_{ii}^q = 0; \quad \omega_q = \frac{2\pi}{(2N_q+1)\Delta q}; \quad \Delta q = 0.1; \quad N_q = 6; \\ & q^i = q_{\min} + \Delta q \cdot (i-1); \quad q_{\min} = -\Delta q \cdot N_q; \end{aligned} \tag{4}$$

Table 1
Frequency values of the PWD normal vibrations calculated at MP4/Aug-cc-pVTZ level of theory with C_2 symmetry restriction.

Level of theory/symmetry of configuration		MP4/Aug-cc-pVTZ/C_2	
Mode number	Modes specification	Symmetry	Harm. freq.[cm^{-1}]
ν_1	Twist H_2O s(d)	A	165.3
ν_2	Wagging H_2O + Stretching O–H–O as(d)	B	344.7
ν_3	Wagging H_2O s(d)	A	460.5
ν_4	Rock + twist H_2O + Bending O–H–O s(d)	B	533.4
ν_5	Rock + twist H_2O + Bending O–H–O as(d)	A	541.8
ν_6	Stretching O–O s(d)	A	623.5
ν_7	Stretching O–H–O + Wagging H_2O as(d)	B	859.8
ν_8	Bending O–H–O as(d)	B	1477.5
ν_9	Bending O–H–O s(d)	A	1557.7
ν_{10}	Bending H–O–H s(d)	A	1713.9
ν_{11}	Bending H–O–H as(d)	B	1763.9
ν_{12}	Stretching O–H s(m) as(d)	B	3726.7
ν_{13}	Stretching O–H s(m) s(d)	A	3733.6
ν_{14}	Stretching O–H as(m) as(d)	B	3823.3
ν_{15}	Stretching O–H as(m) s(d)	A	3823.7