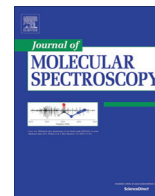




Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Effects of deuteration of the methyl and phenyl hydrogens on the rotational spectrum of anisole-water

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ARTICLE INFO

Article history:

Received 1 February 2017

In revised form 3 April 2017

Accepted 14 April 2017

Available online xxxxx

Keywords:

Hydrogen bond

Isotopic effects

Molecular beams

Molecular complexes

Molecular dynamics

ABSTRACT

The role of non-covalent interactions in determining the structure of the 1:1 anisole-water molecular complex has been investigated by the analysis of the rotational spectra of the complex formed by the $C_6H_5OCD_3$ and $C_6D_5OCH_3$ deuterated species of anisole recorded with pulsed jet Fourier transform microwave spectroscopy. The deuteration of the methyl and phenyl hydrogens does not affect the structure and the internal dynamics of the complex, differently from the deuteration of the water moiety, which leads to large isotopic effects (Giuliano et al., 2005).

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1. Introduction

Water adducts of organic molecules have been widely studied to help the understanding of the solvation processes in aqueous environments and the effects of molecular interactions in gas-phase reactions [1–4]. The different types of complexes of water with organic molecules have been described and classified in a recent paper [5].

Anisole and its 1:1 water complex has attracted much interest in the last years and the structural and dynamical features of the system have been studied with different spectroscopic techniques. These studies mainly focused on the determination of the position of the water molecule with respect to the anisole plane and on the water internal motion.

Experiments based on resonant two-photon ionization and IR-UV double-resonance vibrational spectroscopy complemented by MP2/6-31G* ab initio calculations by Reimann and co-workers [6], suggested a non-planar equilibrium structure of the complex, with one water hydrogen atom involved in a O–H...O hydrogen bond (σ type interaction) and the other hydrogen atom free from interactions lying out of the anisole plane.

Further measurements by Becucci et al. [7] using high-resolution laser induced fluorescence spectroscopy assumed a con-

formation of the complex where the water oxygen atom is coplanar to the ring frame of anisole, with a conventional hydrogen bond of water toward the anisole oxygen in both the ground and the S1 first singlet electronic excited states.

Pure rotational spectroscopy provides the most detailed information about the molecular structure, especially through the analysis of different isotopic species [8]. Some time ago, we investigated the anisole-water complex [9] with particular attention to the determination of the position of the two hydrogen atoms in the water moiety. As an unexpected result, our studies described a novel isotopic effect: the conformational change of a hydrogen-bonded adduct upon deuteration of the water hydrogen atoms involved in the hydrogen-bond. A graphical representation of this effect is given in Fig. 1. In that work we assumed the two water hydrogen atoms to be equivalent to each other and to undergo a rapid exchange in order to explain the observed doubling of the rotational lines. In this configuration, both hydrogen atoms point toward the oxygen atom of anisole forming a bifurcated hydrogen bond.

Following our paper, additional high-resolution electronic spectroscopic studies investigated the structure and dynamics of the complex, with particular effort in describing the interaction of the two moieties in the electronic excited state. Ribblett et al. [10] proposed a structure with the water molecule interacting through one of its hydrogen atoms with the oxygen atom of anisole (primary hydrogen bond) and another one through its oxygen atom and the *ortho* hydrogen of the aromatic ring (secondary inter-

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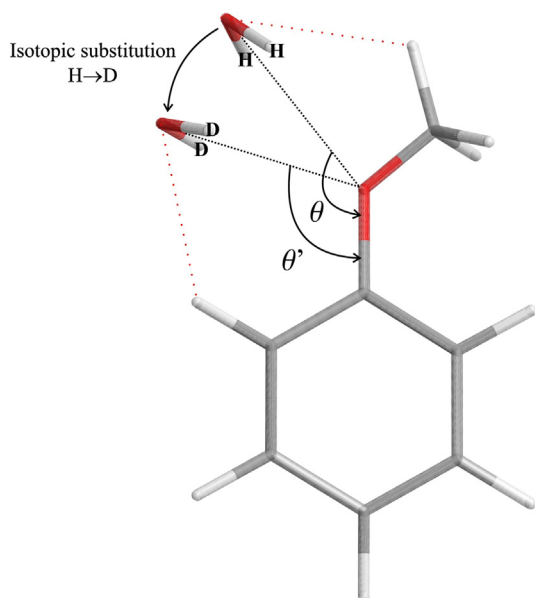


Fig. 1. The deuteration of water produces a conformational change in the anisole–water complex (adapted from Ref. [8]).

action, weak C–H...O bond) for the S_0 ground state. The observed relative blue shift of the two sub-bands of the S_1 - S_0 origin band was explained by a change in the relative magnitude of these two interactions in the S_1 state. To deepen this analysis, Pasquini and co-authors [11] investigated the deuterated anisole–water complex in the first singlet excited electronic state S_1 . They compared their results with high level quantum chemical calculations and with data already available in the literature. They found that the structure of the deuterated complex is more similar to the corresponding structure of the anisole–water complex in the S_1 state than in the S_0 state. They also suggested a mechanism for the proton/deuteron exchange ruled by a bifurcated transition state for the exchange reaction, with both water hydrogen atoms interacting with the anisole oxygen atom. These authors demonstrated that in the S_1 excited state the hydrogen bond in which the water molecule acts as an acid is weaker than in the electronic ground state but it is still the principal interaction between water and the anisole molecules.

These investigations evidenced the importance of the role of the secondary interaction in determining the structure of the anisole–water complex.

Very recently, a rotational study of trifluoroanisole–water was published [12]. In this case, the isotopic effects (conformational change) described for the complex anisole–water were not observed. These effects can be mainly related to the change in the structure of the isolated molecule, in which the substitution of the three methyl hydrogens with fluorine atoms changes the position of the side chain from the in-plane configuration of anisole [13] to a perpendicular shape [14,15].

Motivated by these studies, we decided to investigate the role of the deuteration of the methyl and phenyl hydrogen atoms on the conformational change. We present below also the results obtained by deuteration of water in its complexes with $C_6H_5OCD_3$ and $C_6D_5OCH_3$.

2. Experimental

Anisole- d_3 ($C_6H_5OCD_3$) and anisole- d_5 ($C_6D_5OCH_3$), from now on ANI- d_3 and ANI- d_5 in the text, were supplied by C/D/N ISOTOPES

(Quebec). D_2O (99%) was supplied by Promochem GmbH (Germany), while DOH was generated mixing D_2O and H_2O species in equivalent concentrations.

The rotational spectrum in the frequency region 6–18 GHz was measured using the pulsed jet Fourier transform microwave (PJ-FTMW) spectrometer already described elsewhere [16]. He at a pressure of 2 bar was flowed over a 1:1 mixture of deuterated anisole (ANI) and water (W) and fed through the solenoid valve into the Fabry-Perot cavity, where the mixture reached an estimated rotational temperature of 1–2 K.

3. Results and discussion

For both C-deuterated species, ANI- d_3 and ANI- d_5 , we assigned and measured the rotational spectra of the complexes with H_2O , DOH and D_2O (ANI- d_3 -W and ANI- d_5 -W). In addition, we measured the spectrum of the ANI- d_3 - $H_2^{18}O$ isotopologue.

Similarly to the case of the parent species, the transitions in the rotational spectra of the complexes with H_2O and $H_2^{18}O$ are split into two component lines with an approximate intensity ratio of 1:3. This spectral evidence is generally due to the internal rotation of the water unit around its C_2 axis, which interchanges two equivalent protons ($I = 1/2$, fermions) generating an intensity ratio 1:3 in favour of the asymmetric ($v = 1$) vibrational state. This effects has been observed in similar complexes, such as, for example, phenol–water and indole–water [17,18], and there described. Such a splitting is not observed for the complexes with HDO and D_2O . These observation are in agreement with the proposed path of internal motion of water because in the complex with HDO the proton is not equivalent to the deuteron so that rotation of the water moiety cannot generate two equivalent structures. Differently from this case, in the complex with D_2O the reduced mass of the internal rotation of D_2O is much larger than that of H_2O , and the vibrational splitting is thus much smaller and not resolvable with our experiment.

The standard semirigid rotor Hamiltonian by Watson [19] (I' representation and S reduction) has been used to fit all measured μ_a - and μ_b -type rotational transitions. For the complexes involving H_2O or $H_2^{18}O$, the line frequencies of the two sub-states (labelled $v = 0$ and $v = 1$) have been fitted separately. The spectroscopic constants derived from the fittings for each species are reported in Tables 1 and 2. The complete list of the measured lines is provided as Supplementary Material.

We discuss separately the results for the complexes of water with the methoxy deuterated species ANI- d_3 and the phenyl deuterated ANI- d_5 . The main idea of this work is to verify the role of the secondary interactions in the structural change taking place in the molecular complex upon water deuteration once the hydrogen atoms involved in this secondary interaction (namely the methoxy group and the phenyl ring) are substituted by deuterium. This secondary interaction seems to be involved in the conformational change of the molecular complex upon water deuteration. We will investigate this effect by analysing the spectroscopic constants of the complexes formed by differently deuterated anisole forms, and by calculating the corresponding structures.

From the examination of the value of the rotational constant B of the water deuterated complexes of ANI- d_3 we can observe an anomalous behaviour. Normally, the rotational constants, which are inversely proportional to the moments of inertia, should decrease upon substitution with heavier isotopes, as can be observed for the B value when ^{18}O is substituted for ^{16}O . Nevertheless, similarly to the case of the ANI-W complex, the rotational constant B increases in going from H_2O to HOD or D_2O .

This effect has been explained in Ref. [9] in terms of a decrease of about 10° of the O_W -C- C_{ph} angle (θ in Fig. 1) in going from H_2O to

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