Journal of Molecular Spectroscopy 268 (2011) 47–52

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

The rotational spectra of the fluorobenzene···water and *p*-difluorobenzene···water dimers: Structure and internal dynamics

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ARTICLE INFO

Article history:
Available online 1 April 2011

Keywords:
Fluorobenzene···water complex
p-Difluorobenzene···water complex
Rotational spectra
MB-FTMW spectroscopy
Structure
Internal dynamics

ABSTRACT

The rotational spectra of the weakly hydrogen-bonded complexes of fluorobenzene and *p*-difluorobenzene with water were measured in the frequency range from 3 to 15 GHz using pulsed molecular jet Fourier transform microwave spectrometers in Kiel and in Edmonton. Spectroscopic constants were derived from the spectra of several isotopologues of fluorobenzene···water, i.e. those containing $H_2{}^{16}O$, $H_2{}^{18}O$, HDO, and D_2O, and of *p*-difluorobenzene···water with $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, and D_2O. The structural parameters derived from the determined rotational constants correspond to planar (or nearly planar) structures of the complexes. The internal dynamics of the complexes are discussed with regard to the observed tunneling splittings of the rotational lines, which are a result of the hindered internal rotation of the water subunit.

1. Introduction

The aromatic ring compound benzene and its fluorinated derivatives, $C_6H_{6-n}F_n$ $(1 \leqslant n \leqslant 6)$, are relatively immiscible with water. This hydrophobic behaviour plays an important role in the formation of micelles and biological membranes [1]. Gas-phase spectroscopic studies of microsolvated aromatics, i.e., small aromatic solute···$(H_2O)_n$ clusters, generated in a supersonic molecular expansion, are particularly valuable in providing detailed understanding of the properties of such two-dimensional systems at the molecular level. Special attention to microsolvated benzene has been given in the review by Zwier [2], and a more recent review by Brutschy [3] has emphasized on the discussion of microsolvated fluoro derivatives of benzene.

Microwave spectra of the benzene···water dimer have been reported previously [4–6]. It had been concluded that the water unit is loosely bound to benzene by a weak, so-called π-hydrogen bond, where the water molecule is positioned above the benzene ring plane undergoing nearly free internal rotation with both hydrogen atoms pointing toward the π cloud. There is interest in understanding how the presence of the strongly electronegative fluorine in fluorinated benzenes influences the characteristics of the π-hydrogen bond. Extensive *ab initio* calculations of the dimers of water with fluorobenzene (FB), C_6H_5F, and *p*-difluorobenzene (*p*DFB), *p*-$C_6H_4F_2$ [7], predict the most stable structures to be planar, in contrast to the non-planar π bonded structure of benzene···water. This planar ("σ type") configuration involves a six-membered ring where water acts simultaneously as a proton donor to the F atom and as a proton acceptor to the adjacent H-atom of the aromatic ring. For the *p*DFB···H_2O dimer, the theoretically predicted planar structure has been confirmed by rotationally resolved electronic spectra [8] which also show tunneling splittings as a result of an internal motion of the water moiety within the complex.

In the present work we report the observation and analysis of pure rotational spectra of the FB···water and *p*DFB···water dimers. Molecular jet Fourier transform microwave (MB-FTMW) spectroscopy was utilized in this study to obtain information about the structures and the internal dynamics of these weakly bound complexes in their ground vibronic states. Not only the parent isotopologues were studied, but also several with isotopic substitutions at the water moiety. These additional data allowed a more complete determination of structural parameters which define the orientation of water with respect to the aromatic ring. Information about the internal dynamics of the dimers was obtained from an analysis of the observed splittings of rotational lines, and from *ab initio* and internal rotation modeling calculations.

2. Experimental

High resolution rotational spectra of the FB···water and *p*DFB···water complexes were recorded in the frequency range from about 3 to 15 GHz using two pulsed-jet Fourier transform spectrometers at the Universities of Kiel and Alberta. The

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doi:10.1016/j.jms.2011.03.032

spectrometers are similar to that of the original design of Balle and Flygare [9], but with a coaxial arrangement of the pulsed molecular jet with respect to the microwave resonator axis [10]. Details of the spectrometers have been described elsewhere [11–13].

Commercial samples of FB and *p*DFB (Lancaster) were used without further purification. For the investigation of the dimers containing rare isotopologues of water, isotopically enriched samples of D_2O (Aldrich), $H_2{}^{17}O$, and $H_2{}^{18}O$ (Eurisotop) were used. The HDO sample was prepared by mixing equal amounts of H_2O and D_2O. The sample gas mixtures were prepared by filling an evacuated 2 L stainless steel cylinder first with 12 mbar of H_2O. Then the respective fluorinated benzene was added to a total pressure of 24 mbar to obtain a 1:1 ratio of the two subunits. Finally, neon was added as the carrier gas to a total pressure of about 6 bar. This sample gas mixture was injected into the resonator through a pulsed valve (General Valve Corp., Fairfield, NJ) at a repetition rate of 2 Hz and a typical (reduced) backing pressure of ca. 3.6 bar. Under these conditions, the prepared mixture could be used for several days of intensive measurements.

Normally, the time domain data consisted of 16 k data points, which were recorded at a sample interval of 10 ns. This resulted in a point distance of 6.1 kHz in the frequency domain after Fourier transformation (without zero filling). Because of the coaxial arrangement of molecular expansion and resonator axis, a Doppler splitting (on the order of tens of kHz), which depends on the microwave frequency and the choice of the carrier gas, was observed for every line. The accuracy of the line center frequencies obtained with a peak finder routine is estimated to be 1–2 kHz.

3. Spectral assignment and analyses

Initial attempts to record and assign rotational spectra of the complexes FB···H_2O and *p*DFB···H_2O were based on the *ab initio* predictions of Tarakeshwar et al. [7] for both planar (σ-) and non-planar (π-) configurations. No signals which could be assigned to the corresponding dimers were initially detected, presumably because of an improper sample preparation resulting in too high a water content (by passing a mixture of 0.5% FB or *p*DFB in neon through a reservoir with water). Better predictions of transition frequencies in the microwave region based on the rotationally resolved UV spectra of *p*DFB···H_2O [8,14], allowed the detection of the corresponding lines after a sufficiently high number (>4000) of averaging cycles. Subsequently, the sample preparation was optimized, and the signal to noise ratio improved by about two orders of magnitude.

For both FB···H_2O and *p*DFB···H_2O, *a*- and *b*-type electric dipole transitions were measured, whereas no *c*-type transitions could be detected. This is compatible with the theoretically predicted planar configuration and the structure analyses described in the following section. The corresponding geometries of both complexes, together with their principal inertial axes systems are shown in Fig. 1a and b, respectively.

Besides the Doppler splitting, each line is additionally split into a weak and a strong component with an intensity ratio of 1:3. An example transition of FB···H_2O is shown in Fig. 2. As will be discussed in more detail in Section 5, this splitting can be attributed to an internal rotation of the water moiety within the complex which interchanges the bonded and non-bonded hydrogen nuclei. Accordingly, the two components correspond to the rotational spectra of the two lowest internal rotation tunneling states (O^+ and O^-), with different spectroscopic constants and different spin statistical weights.

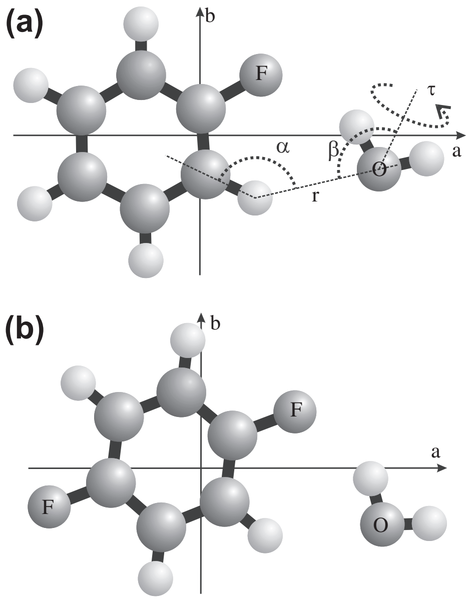

Fig. 1. Structure and *a*-, *b*-principal inertial axes of: (a) fluorobenzene···water and (b) *p*-difluorobenzene···water.

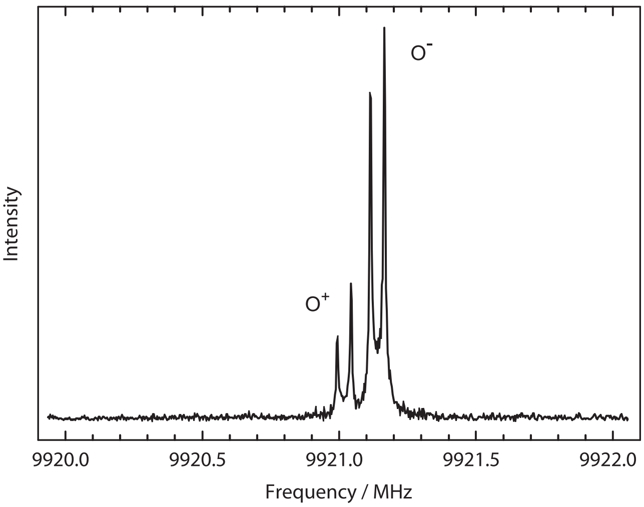

Fig. 2. Rotational transition $4_{04} \leftrightarrow 5_{05}$ of fluorobenzene···$H_2{}^{16}O$ with O^+ and O^- component lines and Doppler doublets. Measuring conditions: excitation pulse length: 0.6 μs; excitation power: 50 mW, 10 ns sample interval, 100 averaging cycles. The spectrum was obtained from 16 k time domain data points with 16 k zero filling.

Since the tunneling states are associated with two different nuclear spin states, we fitted the rotational lines for each tunneling state separately on the basis of a centrifugally distorted asymmetric rotor. The spectroscopic constants were fitted using the program SPFIT by Pickett [15,16]. Watson's A-reduction Hamiltonian [17] in the I^r representation was used and fourth order centrifugal distortion terms were included. The resulting spectroscopic constants are collected in Tables 1 and 2 for FB···H_2O and *p*DFB···H_2O, respectively. Since only lines with values of the limiting prolate top quantum number K_a of 0 and 1 were detected for FB···H_2O, the centrifugal distortion constant Δ_K could not be determined and was thus fixed to zero in the fit. The full set of quartic centrifugal distortion constants was determined from the observed lines of *p*DFB···H_2O which include also lines with $K_a = 2$.

For the complex of fluorobenzene with water, the spectra of the FB···$H_2{}^{18}O$, FB···DHO and FB···D_2O isotopologues were also