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Hydrated Complexes of Atmospheric Interest: Rotational Spectrum of Diacetyl−Water[†]

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The rotational spectrum of the molecular complex diacetyl−water has been measured by pulsed jet Fourier transform microwave (FTMW) spectroscopy. The water molecule acts as an electrofore and induces a dipole moment when combined with nonpolar diacetyl. Only one conformer has been observed, corresponding to the global minimum. Its shape is unambiguously established: the water moiety is linked asymmetrically to the organic molecule; it behaves as a proton donor to one of its oxygen atoms and interferes with the internal rotation of adjacent methyl group through a C−H···O interaction. Each rotational transition appears as a quintuplet, due to the internal rotation of the two methyl groups, which are nonequivalent in the adduct. From the analysis of the observed splittings, the V_3 barriers to the internal rotation of the two methyl groups have been determined to be 3.81(2) and 4.11(2) kJ/mol, respectively.

Introduction

Aromatic hydrocarbons, which are released in the atmosphere in urban and industrial areas, lead to formation, upon photooxidation, of small α-dicarbonyl molecules, such as glyoxal, methylglyoxal, and diacetyl.[1] These molecules, similarly to other molecules containing carbonyl groups, can play an important role in atmospheric chemistry. For example, it has been shown that formaldehyde, acetaldehyde, and acetone are important sources of HO_x in the troposphere[2−4] and that polluted water droplets contain high concentrations of carbonyl compounds.[5,6]

The complexation of atmospheric species with water dramatically changes the kinetics of their decomposition.[7] For this reason it is important to study the binding energies, the conformations, and the structures of their adducts with water.

As to the experimental studies of complexes of α-dicarbonyl molecules with water, only a Fourier transform infrared (FTIR) matrix isolation spectroscopy is available.[8] The authors of that study could observe infrared peaks in the regions of the ν (OH) stretching of water and of the ν (C=O) stretching of α-dicarbonyl. However, trial assignments of the measured peaks to the proper conformer of the adduct were based on MP2 calculations with 6-311++G(2d,2p) basis set, performed in the same paper.[8]

Pure rotational spectroscopy has been very successful in determining the conformation and energetics of hydrated complexes. However, although this technique has been extensively applied to investigate conformations and structures of complexes of ethers with water,[9−16] little attention has been dedicated to the adducts of water with aldehydes, and their rotational spectra have been investigated only in a couple of cases,[9] such as formaldehyde−water[17] and cyclobutanone−water.[18]

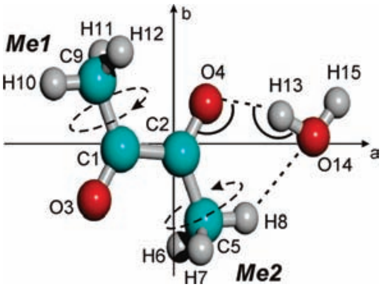

Figure 1. Configuration, principal axes, atom numbering, relevant internal motions, and structural parameters of the most stable conformer of DAC−W. The water molecule can be bound to each of the two different lone pairs of one of the two equivalent oxygen atoms of DAC. The two methyl groups are no longer equivalent.

No microwave (MW) investigations are available for complexes of α-dicarbonyl molecules with water. Since, in ref 8, the theoretical calculations gave almost the same binding energies for three conformers of diacetyl−water (DAC−W, see Figure 1), we decided to investigate its pulsed jet Fourier transform microwave (FTMW) spectrum, in order to unambiguously establish its most stable conformation. Due to its center of symmetry, DAC is a nonpolar molecule, whereas its adduct with water is polar because water acts as an electrofore.

Experimental Section

A commercial sample of DAC, supplied by Aldrich, has been used without further purification. Molecular clusters have been generated in a supersonic expansion, at conditions optimized for 1:1 cluster formation. The details of the COBRA-FTMW spectrometer,[19] which covers the range 6.5−18 GHz, have been described previously.[20] He at a total pressure of 2.5 bar was flowed over the 1:1 mixture of water and DAC at room temperature and expanded through the solenoid valve (General Valve, series 9, nozzle diameter 0.5 mm) into the Fabry−Pérot cavity where the mixture reached an estimated rotational temperature of 1−2 K. The frequencies were determined after Fourier transformation of the 8K data points time domain signal, recorded with 100 ns sample intervals. Each rotational transition is split by Doppler effect due to the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is

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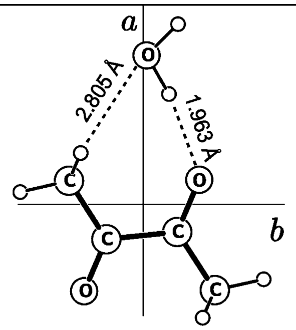
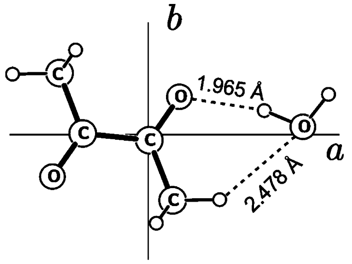
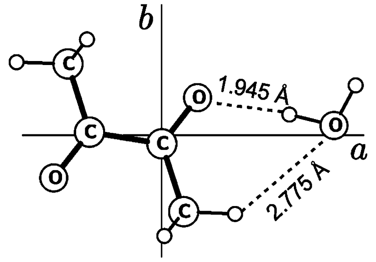
TABLE 1: Sketches and Calculated Rotational Constants of the Three More Stable Conformations of DAC−W (from the MP2/6-311++G(2d,2p) Calculations of Ref 8)

	 I	 II	 III
ΔE/ kcal mol^{-1}	-2.93	-3.03	-2.83
A/ MHz	3383.5	4820.4	4667.8
B/ MHz	1555.1	1232.5	1204.6
C/ MHz	1079.4	993.4	968.7
$\angle(a,i)_{\mathrm{Me1}}$/ °	32.9	68.1	72.4
$\angle(a,i)_{\mathrm{Me2}}$/ °	32.6	67.8	72.1

calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

Rotational Spectrum

In the above-mentioned MP2/6-311++G(2d,2p) calculations,[8] Mucha and Mielke optimized three different structures, which are sketched in Table 1, together with the binding energies and the calculated parameters relevant to the rotational spectra, the rotational constants and the angles $\angle(a, i)$ that the internal rotation axes of the two methyl groups form with the a-principal axis. These parameters were not reported in ref 8 so that we calculated them from the geometries there given. In all the three cases the water molecule lies in the plane of symmetry of DAC, and the intermolecular hydrogen bond is between one of the DAC oxygen atoms and one of the water hydrogen atoms. The first two structures differ because the water may be zusammen (II) or entgegen (I) with respect to the methyl group attached to the same C=O group to which water is linked. In the third one the water is slightly reoriented with respect to the zusammen configuration. In the calculations, conformer II resulted to be the most stable and the conformational energy differences with the other two turned out to be small ($E_{\mathrm{I}} - E_{\mathrm{II}} = 0.42$ kJ mol^{-1}, $E_{\mathrm{III}} - E_{\mathrm{II}} = 0.84$ kJ mol^{-1}). These energy differences could be due to a very weak interaction between the water oxygen and one of the hydrogen atoms of the adjacent CH_3 group. This occurrence seems to be more plausible in the second conformer as suggested by the fact that for this case the distance between the aforesaid atoms resulted shorter than for the other two ($R(O_w\cdots H{-}C) = 2.81, 2.48, 2.77$ for I, II, and III, respectively).

On the basis of the theoretical values of the rotational constants, we searched for the spectrum of DAC−W with a FTMW spectrometer. The assignment of the measured transitions was facilitated by the fact that, apart a few lines of the dimer of water, the only observable spectrum in the DAC/water mixture is that of the adduct, since the DAC electric dipole moment is zero by symmetry. We found five μ_a-type R bands, typical of a near-prolate top, evenly spaced by the $B + C$ value and with J in the range from 3 to 8. We could measure single transitions with K_a ranging from 0 to 2. Finally we could measure some μ_b-type lines.

All transitions have a complex structure, due to the coupling of the internal rotation of the two methyl groups with the overall rotation of the complex. In the case of DAC, the molecular symmetry (MS) group G_{36} introduced for dimethylacetylene[21] and later given for acetone[22] is appropriate. However, in DAC−W, the two methyl groups are not equivalent and the rotational−torsional energy levels of the adduct relate to the MS group G_{18}, as in the case of ^{13}C-difluorodimethylsilane[23] or dimethoxymethane−water.[24] The sublevels generated by the internal rotations of the two (nonequivalent) methyl groups are classified according to their symmetry as A_1, E_1, E_2, E_3, and E_4.[23] Correspondingly, the rotational transitions are split in quintets, whose component labeling scheme coincides to the previous one as no transition is allowed between states of different symmetry. Such a pattern is shown, as an example, in Figure 2 for the $5_{1,4}-4_{1,3}$ transition.

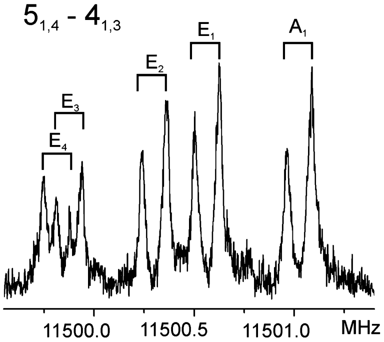


Figure 2. The $5_{1,4}-4_{1,3}$ transition, showing the five (A_1, E_1, E_2, E_3, E_4) components originated by the internal rotation of the two nonequivalent methyl groups of DAC−W.

TABLE 2: Spectroscopic and Internal Rotation Constants of DAC−W (S-Reduction, I^r Representation)

		internal rotation parameters		
			Me1	Me2
A/MHz	4787.344(3)[a]			
B/MHz	1213.1362(2)			
C/MHz	981.2839(2)	V_3/kJ mol^{-1}	3.81(2)	4.11(2)
D_J/kHz[b]	0.304(1)	I_α/uÅ^2	3.22(2)[c]	3.22(2)[c]
D_{JK}/kHz	2.75(2)	$\angle(a, i)$/deg[d]	67.4(1)	66.3(1)
d_1/kHz	−0.057(1)	$\Delta_{\pi 2K}$/MHz	−0.42(4)	−0.14(5)
d_2/kHz	−0.011(1)	Δ_{c3J}/MHz	−2.80(7)	1.4(1)
σ/kHz[e]		4		
N[f]		127		

[a] Errors in parentheses are expressed in units of the last digit. [b] D_K is fixed to zero as it is undetermined from the fit. [c] The I_α parameters of the two methyl groups have been fixed to a common value. [d] The values of the $\angle(b, i)$ and of the $\angle(c, i)$ parameters are the complement to 90° of $\angle(a, i)$, and 90° (from the planarity of the mainframe), respectively. [e] Root-mean-square deviation of the fit. [f] Number of fitted lines.

The experimental frequencies, given as Supporting Information, have been fitted with computer program XIAM,[25] suitable to take into account the effects of the internal rotations of the methyl groups within the combined axis method (CAM). In the CAM approach, a global fit to the absolute line positions of A_1, E_1, E_2, E_3, and E_4 components is performed. A "rigid" limit set of rotational constants has been determined common to all A_1, E_1, E_2, E_3, and E_4 sublevels. In addition, four quartic centrifugal distortion constants, the two V_3 barriers, the I_α moments, the angles $\angle(a, i)$ that the axis of rotation of the tops form with the a-principal axis of inertia and two internal rotation−overall rotation interaction distortion constants, have been determined. The quartic centrifugal distortion constants correspond to the S-reduction and I^r representation.[26] Spectroscopic constants obtained are given in Table 2.

Conformation and Structure

Just by comparison of the experimental rotational constants of Table 2 to the theoretical values of Table 1, it is easy to see that the observed spectrum corresponds to conformer II. Also the $\angle(a, i)$ internal rotation angles confirm the conformational assignment. The inertial defect is calculated to be −7.137 uÅ^2. This value is slightly higher than expected for two methyl groups (ca. −6.4 uÅ^2), but the difference is probably due to the contributions from the out of plane skeletal torsion. The rotational constants of diacetyl determined from a rovibronic spectrum[27] supply a value for the inertial defect of −7.4 uÅ^2, but the uncertainty is not given. However, it is very close to the value of DAC−W, suggesting water to lie in the plane of the mainframe of bare DAC.

The structure of the complex is given in Table 3. Most of parameters come from the ab initio values,[8] while a partial r_0 refinement was obtained from the three available experimental rotational constants. The two parameters, H13···O4 and O14H13O4 of Figure 1, were indeed adjusted to reproduce the experimental data. The results, shown in bold in Table 3, were obtained constraining them into a 5% confidence interval of the ab initio values and keeping fixed all the other geometrical parameters. The calculated rotational constants with the structure of Table 3 are A = 4787.4, B = 1213.9, and C = 978.9 MHz, respectively. The maximum discrepancy is 1.4 MHz for the rotational constant C.

TABLE 3: Effective Structure (Which Reproduces the Rotational Constants) of the Observed Conformer of DAC−W, Based on the MP2/6-311++G(2d,2p) Geometry of Ref 8[a]

bond lengths/angstroms		angles/deg	
C1−C2	1.541	C2C1O3	119.0
C1−O3	1.220	C1C2O4	118.7
C1−C9	1.501	C1C2C5	117.0
C2−O4	1.225	C2C1C9	116.7
C2−O5	1.496	C2C5H8	110.4
C5−H8	1.083	C2C5H6(H7)	109.3
C5−H6(H7)	1.088	C1C9H10	109.5
C9−H10	1.083	C1C9H11(H12)	109.8
C9−H11(H11)	1.088	H13O4C2	115.2
O14−H13	0.966	O14H13O4	**166.3(4)**[b]
O14−H15	0.958	H13O14H15	105.1
H13···O4	**1.981(4)**[b]	H8C2−C5H6(H7)[c]	122.0
H8···O14	**2.56(1)**[d]	H10C1−C9H11(H12)[c]	121.6

[a] See Figure 1 for atom numbering. [b] The parameters in bold have been fitted (error in parentheses) to reproduce the experimental rotational constants. Their ab initio values are H13···O4 = 1.965 Å and O14H13C2 = 160.8°, respectively. [c] These are the only nonzero dihedral angles, once assumed that water is in the plane of the mainframe of DAC. [d] Derived parameter.

Conclusions

The configuration of the global minimum of the DAC−W complex has been determined from the analysis of the FTMW spectra of the complex. The water moiety is linked in an asymmetric way to DAC, forming both a strong O···H−O and a weak O···H−C hydrogen bond. The barriers to internal rotation of the two methyl groups are V_3(Me1) = 3.81(2) and V_3(Me2) = 4.11(2) kJ mol^{-1}. The geometry related $\angle(a, i)$ angles of the two tops have nearly equal values so that the assignment of the V_3 values to the two methyl groups is not straightforward. However, it appears reasonable to assign the higher barrier to the Me2 top (see Figure 1), the one whose internal rotation is further hindered by its interaction with the water molecule. A similar increase of the V_3 barrier of the methyl group interacting with water was observed in the case of dimethoxymethane−water,[24] for which this assignment was supported by the values of the fitted geometrical parameters. From the obtained V_3 barriers the far-infrared transitions due to the methyl torsions are predicted to occur at 123 and 127 cm^{-1}, respectively, in agreement with the ab initio values.[8]

The fact that we could not detect other conformers of the complex, which, according to the ab initio calculations, are expected to have similar energies, can be attributed to the interconformational relaxation to the global minimum, which takes place when different conformers are separated by low interconversion barriers.[28]

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Supporting Information Available: Table of transition frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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