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Noncovalent Interactions and Internal Dynamics in Dimethoxymethane–Water

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Dedicated to Professor Paolo G. Favero on the occasion of his 80th birthday

Abstract: The millimeter-wave absorption and Fourier transform microwave spectra of five isotopologues of the 1:1 adduct of dimethoxymethane–water have been measured in supersonic expansions. Each rotational transition appears as a quintuplet, due to the internal rotation of the two methyl groups, which are nonequivalent in the adduct. The water moiety, linked asymmetrically to dimethoxymethane, behaves as a proton donor to one of its oxygen atoms and interferes with the internal rotation of the farther methyl group through a C–H···O interaction. 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 6.83(8) and 6.19(8) kJ mol^{-1}. The hydrogen bond structural parameters have been determined, the O–H···O and C–H···O distances being 1.93(1) and 2.78(4) Å, respectively.

Keywords: ab initio calculations · hydrogen bonds · molecular complexes · molecular dynamics · noncovalent interactions · rotational spectroscopy

Introduction

The investigation of several complexes of organic molecules (OM) with water (W) by rotationally resolved spectroscopy provides information on their conformation, structure, internal dynamics, and energetics. When water is linked as a proton acceptor, as in the case of indole–W,[1] phenol–W,[2–4] and species Ic (with a N–H···O linkage) of formamide–W,[5] the W subunit is relatively free to rotate with respect to the OM. As a consequence, splittings are observable in the pure rotational spectra,[1,3] from which information on the potential-energy surface is obtained. When water acts as a proton donor towards weak proton acceptors, such as a fluorine or chlorine atom, or a π system, the water moiety has a considerable dynamic freedom, which still produces features in the microwave (MW) spectrum, as in the cases of difluoromethane–W,[6] chlorofluoromethane–W,[7] and benzonitrile–W.[8] Finally, when water acts as a proton donor and forms strong hydrogen bonds, such as O–H···O,[9–12] O–H···N,[5,13–16] or O–H···S,[17] the water moiety is blocked and no splitting due to its internal dynamics is observed. Some exceptions have been observed, however: 1) in the case of dimethylether–W,[18] the W molecule tunnels between the two lone pairs of the ether oxygen, generating large tunnelling splittings; 2) in anisole–W,[19] the W moiety is delocalized while forming secondary interactions with the adjacent methyl or phenyl hydrogen atoms, allowing tunnelling of the water hydrogen atoms.

Dimethoxymethane (DMM) possesses two equivalent oxygen atoms, each of them with two nonequivalent lone pairs. This could generate two different isomers of the 1:1 adduct DMM–W, as shown in Figure 1. In addition, the dynamics of the internal rotation of the two methyl groups, equivalent in the DMM monomer,[20] are expected to change in the adduct. Rotational spectroscopy in supersonic jets is suitable for solving this kind of problem, and for this reason we report here millimetre-wave absorption and Fourier transform microwave spectra of DMM–W in supersonic expansions.

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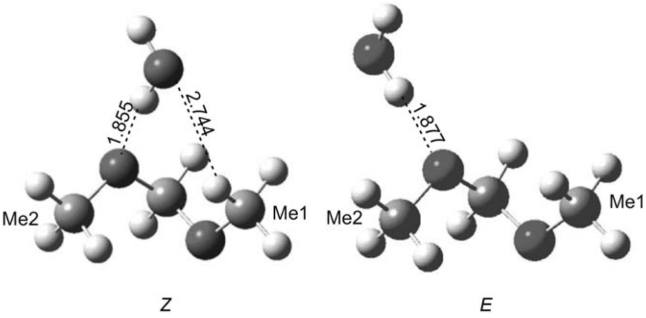

Figure 1. The water molecule can be bound to each of the two different lone pairs of one of the two equivalent oxygen atoms of DMM, generating *zusammen* (Z) or *entgegen* (E) adducts. The two methyl groups are no longer equivalent.

Results

Preliminary model calculations: Calculations on the stable conformations of DMM–W were carried out at the MP2/6–311++G** level of approximation by using the Gaussian 03 software package.[21] Two different structures were optimized without any constraint. In both of them the intermolecular hydrogen bond is between one of the oxygen atoms of dimethoxymethane and one of the water hydrogen atoms. Moreover, the water lies almost in the plane perpendicular to the COC frame containing the oxygen atom involved in the hydrogen bond.

The two structures differ because the water may be *zusammen* (Z) or *entgegen* (E) with respect to the farther methyl group (see Figure 1).

In the calculations, conformer Z was found to be the most stable, with a conformational energy difference ΔE $(=E_E-E_Z)=4.2\ \mathrm{kJ\,mol^{-1}}$. Introducing the basis-set superposition error (BSSE) corrections,[22,23] this value decreases to $\Delta E_{\mathrm{BSSE}}=2.2\ \mathrm{kJ\,mol^{-1}}$. This energy difference could be due to a secondary interaction between the water oxygen and one of the methyl hydrogen atoms which occurs only in conformer Z. Only the Z and E forms of the DMM–W complex were considered in our ab initio calculations. Other adducts could be formed between water and high-energy conformers of DMM (see reference [20] and references therein).

Abstract in Italian: *Sono stati misurati gli spettri rotazionali a trasformata di Fourier in espansione supersonica di cinque isotopologhi dell'addotto dimetossimetano-acqua. Ciascuna transizione rotazionale appare come un quintupletto, a causa della rotazione interna dei due gruppi metilici, che nell'addotto non sono equivalenti. La molecola d'acqua, legata in modo asimmetrico al dimetossimetano, agisce come proton donatore nei confronti di un ossigeno del dimetossimetano, ed interferisce con il metile piu' lontano tramite un'interazione C−H···O. Dall'analisi degli splittings osservati sono state determinate le barriere* V_3 *per la rotazione interna dei due metili, 6.83(8) e 6.19(8)* $\mathrm{kJ\,mol^{-1}}$. *Sono stati determinati i parametri strutturali dei legami a ponte idrogeno, e le distanze O−H···O e C−H···O sono 1.93(1) e 2.78(4) Å, rispettivamente.*

The calculated dissociation energy ranges from 31.1 to $21.2\ \mathrm{kJ\,mol^{-1}}$ with basis set superposition error correction for conformer Z, and similarly from 26.8 to $18.9\ \mathrm{kJ\,mol^{-1}}$ for conformer E.

The calculated rotational constants are reported in Table 1 together with the estimated dipole moment components and the energy values mentioned above.

Table 1. Ab initio (MP2/6–311++G**) rotational constants, dipole moment components, relative energies and dissociation energies of the two conformers of DMM···W.

	Z	E
A [MHz]	3199.9	5021.6
B [MHz]	2402.8	1522.7
C [MHz]	1640.9	1338.3
μ_a [D]	0.53	2.11
μ_b [D]	1.71	0.09
μ_c [D]	0.80	1.72
μ_{tot} [D]	1.96	2.72
E_{conf} [$\mathrm{kJ\,mol^{-1}}$]	0[a]	4.2 (2.2)[b]
E_{diss} [$\mathrm{kJ\,mol^{-1}}$]	31.1 (21.2)[b]	26.8 (18.9)[b]

[a] Absolute energy: −323.51230 E_h. [b] Values in parentheses include basis set superposition error corrections.

Rotational spectrum: Based on the theoretical values of the rotational constants, we first searched for the spectrum of DMM–W with a pulsed-jet absorption millimeter wave (PJ-AMMW, see Experimental Section) spectrometer, which allows a fast scan. We identified some coalescing, μ_b and μ_c, high K_{-1} asymmetry, degenerate R-type transitions (e.g. $10_{10}\leftarrow 9_9$). They were very broad lines, which could be assigned to conformer Z. From the obtained approximate rotational constants, we made a prediction for the measurements of the spectrum with Fourier transform microwave spectroscopy (FT-MW), a technique more sensitive and with a higher resolving power (see Experimental Section). In the MW frequency region we assigned several μ_a, μ_b, and μ_c type transitions, with the μ_b transitions being 3–4 times stronger (taking into account the line strengths and the MW power optimization) than the other two types. This observation is in agreement with the calculated values of the dipole moment components of conformer Z.

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. The rotational–torsional energy levels of DMM, when internal rotation tunnelling is allowed for, relate to the molecular symmetry (MS) group G_{36} introduced for dimethylacetylene,[24] and later given for acetone.[25] The torsional wavefunctions, $|k_1k_2\rangle=|00\rangle$, $|\pm1\pm1\rangle$, $|\pm1\mp1\rangle$ and $|\pm10\rangle$ or $|0\pm1\rangle$, can be classified according to their symmetry as A_1, E_1, E_3, and G, respectively. The signed integers k_i, often also denoted as m or l, represent the torsional quantum numbers of the two internal rotors. In the case of DMM–W the two methyl groups are no longer equivalent, so that the rotational–torsional energy levels of the adduct, when internal rotation tunnelling is allowed for, relate to the MS group G_{18}. This was shown recently in the case of ^{13}C-difluorodimethylsilane,[26] in which the molecular symmetry is modified due to the asymmetric isotopic substitution. In the case of the G_{18} MS group, the torsional wavefunctions, $|k_1k_2\rangle=|00\rangle$, $|\pm1\pm1\rangle$, $|\pm1\mp1\rangle$, $|\pm10\rangle$ and $|0\pm1\rangle$, can be symmetry classified as A_1, E_4, E_3, E_2, and E_1, respectively. Correspondingly, the rotational transitions are split into quintets, with components A_1, E_1, E_2, E_3, and E_4. Such a pattern is shown, as an example, in Figure 2 for the $3_{3,1}$–$2_{2,0}$ transition.

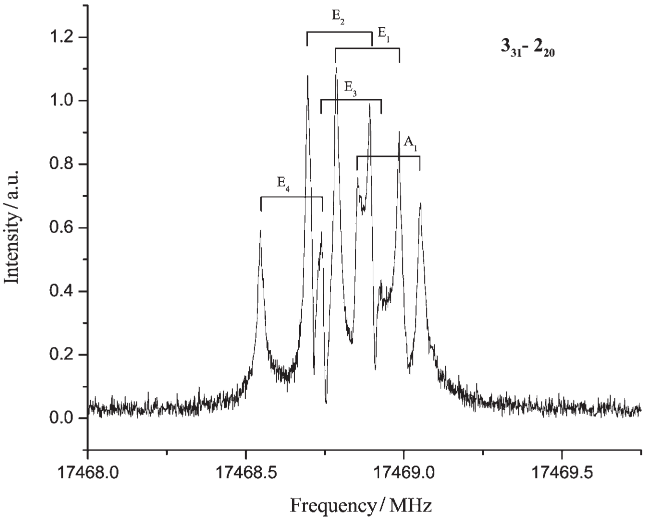

Figure 2. The $3_{3,1}$–$2_{2,0}$ transition, showing the five (A_1, E_2, E_3, E_4, E_5) components resulting from the interaction between the overall rotation and the internal rotation of the two non-equivalent methyl groups of DMM–W.

The experimental frequencies, given as Supporting Information, have been fitted with the computer program XIAM,[27] which takes into account the effects of the internal rotations of the methyl groups within the combined axis method (CAM). The results are shown in Table 2. In the CAM approach, a global fit to the absolute line positions of A_1, E_1, E_3, E_2, and E_4 components is performed. A "rigid" limit set of rotational constants has been determined common to all A_1, E_1, E_3, E_2, and E_4 sublevels. In addition, all quartic centrifugal distortion constants, the two V_3 barriers, the I_α moments of inertia and the angles $\sphericalangle gi$ ($g=a$, b, c) have been determined. The quartic centrifugal distortion constants correspond to the A-reduction and I^r-representation.[28] No lines of relevant intensity were left unassigned in the spectrum.

The FT-MW spectrum was assigned and measured for four additional isotopologues of DMM–W, namely DMM–$H_2{}^{18}O$, DMM–D_2O, DMM–HDO, and DMM–DHO. All measured transitions are given as Supporting Information, while the spectroscopic constants of all isotopologues are given in Table 2.

Table 2. Spectroscopic constants for the five isotopologues of DMM···W (A-reduction, I^r representation).

	DMM···H_2O	DMM···D_2O	DMM···H_2O^{18}	DMM···DOH	DMM···HOD
A [MHz]	3129.4913(4)[a]	3125.655(4)	3119.879(3)	3132.918(7)	3122.57(1)
B [MHz]	2377.1122(4)	2231.603(7)	2235.451(3)	2340.6485(8)	2263.550(2)
C [MHz]	1608.0399(4)	1541.022(1)	1539.430(2)	1592.2421(7)	1555.268(1)
Δ_J [kHz]	5.58(1)	4.6(2)	4.54(9)	5.63(2)	4.33(7)
Δ_{JK} [kHz]	9.68(5)	8.6(2)	15.3(2)	9.0(4)	13.1(9)
Δ_K [kHz]	−6.22(4)	−6.22[b]	−13.1(8)	−6.22[b]	−6.22[b]
δ_J [kHz]	2.093(5)	1.7(1)	1.61(4)	2.093[b]	1.53(3)
δ_K [kHz]	6.28(4)	6.28[b]	7.3(5)	6.28[b]	6.28[b]
H_{kJ} [Hz]	0.63(5)	0.63[b]	0.63[b]	0.63[b]	0.63[b]
Me1					
V_3 [kJ mol^{-1}]	6.83(8)	6.7(3)	6.9(3)	6.83[b]	7.0(4)
I_α [uÅ^2]	2.88(4)	3.0(2)	2.9(1)	2.88[b]	2.8(2)
$\sphericalangle(a\ i)$ [°]	60.5(2)	51(3)	57.1(9)	63(2)	57(4)
$\sphericalangle(b\ i)$ [°]	37.9(3)	48(4)	41(1)	36(2)	42(4)
$\sphericalangle(c\ i)$ [°]	68.4(3)	67(3)	69(1)	68.7(8)	68(3)
Me2					
V_3 [kJ mol^{-1}]	6.19(8)	6.0(2)	6.1(1)	6.19[b]	6.0(2)
I_α [uÅ^2]	3.3(4)	3.4(1)	3.32(6)	3.3[b]	3.4(1)
$\sphericalangle(a\ i)$ [°]	71.2(1)	71(6)	66(1)	68(3)	66(6)
$\sphericalangle(b\ i)$ [°]	48.9(4)	53(3)	54(1)	52(2)	51(3)
$\sphericalangle(c\ i)$ [°]	47.0(4)	44(3)	46(1)	46(2)	48(3)
σ/σ_{exptl}[c]	0.61	1.10	0.86	0.86	1.02
N[d]	203	57	82	31	43

[a] Errors in parentheses are expressed in units of the last digit. [b] Fixed to the normal species value as it is undetermined from the fit. [c] Reduced standard deviation of the fit, relative to measurement errors of 5 and 50 kHz for the MB-FTMW and free jet absorption millimetre wave spectrometer, respectively. [d] Number of fitted transitions.

Conformation and structure: Just by comparison of the experimental rotational constants of Table 2 to the theoretical values of Table 1, it is evident that the observed spectrum corresponds to conformer *Z*. Two additional pieces of information, the $\sphericalangle gi$ internal rotation angles (see the previous section and Table 2) and the r_s coordinates[29] of the substituted atoms, confirm the conformational assignments. The experimental values of these quantities are compared in Table 3 to the theoretical values (corresponding to r_e coordinates) of the two conformers.

In this case, it is difficult to obtain reliable interatomic distances from the r_s coordinates of the water atoms. The $|b|$ coordinate of the hydrogen-bonded hydrogen atom and the $|c|$ coordinate of the oxygen atom have, indeed, imaginary values. Caution is needed in considering the r_s position of a hydrogen atom involved in a hydrogen bond, because the H→D isotopic substitution produces a shrinking of the distance between the heavy atoms involved in the hydrogen

Table 3. Comparison between the experimental and the ab initio (MP2/6–311++G**) values of the $\sphericalangle(gi)$ angles characterizing the internal rotations of the methyl groups and of the Cartesian coordinates (in the principal axes system of the complex) of the water moiety of DMM···H_2O.

	Exptl	Theory	
		conf. Z	conf. E
angles $\sphericalangle(g\ i)$ of Me			
$\sphericalangle(ai)$ [°]	60.5(2)	57.3	74.0
$\sphericalangle(bi)$ [°]	37.9(3)	38.0	58.7
$\sphericalangle(ci)$ [°]	68.4(3)	72.9	36.0
angles $\sphericalangle(g\ i)$ of Me2			
$\sphericalangle(ai)$ [°]	71.2(1)	75.8	88.5
$\sphericalangle(bi)$ [°]	48.9(4)	49.5	2.7
$\sphericalangle(ci)$ [°]	47.0(4)	44.0	87.8
cartesian coordinates of the water oxygen			
a [Å]	±2.609(2)	2.545	3.088
b [Å]	±0.576(9)	−0.706	0.756
c [Å]	0.10i	0.012	−0.027
cartesian coordinates of the H_{bond} water hydrogen			
a [Å]	±1.825(2)	1.819	2.180
b [Å]	0.44i	−0.082	0.436
c [Å]	±0.09(2)	0.163	−0.136
cartesian coordinates of the H_{free} water hydrogen			
a [Å]	±3.238(2)	3.269	3.256
b [Å]	±0.46(1)	−0.347	1.240
c [Å]	±0.44(1)	0.529	−0.837

bond (Ubbelhode effect[30]). As for the imaginary $|c|$ value for the water oxygen atom, this is plausibly due to the large amplitude motion that the water moiety undergoes in the complex.

A partial r_0 structure was calculated from the experimental rotational constants of the five isotopologues. The geometries of DMM and water were kept constant at their ab initio values in the complex, while fitting the r_{O2-Ow}, $\sphericalangle O_wO_2C_3$, $\sphericalangle O_wO_2{-}C_3O_4$, and $\sphericalangle H_{free}O_w{-}H_{bond}O_2$ parameters of Figure 3. The derived, but more significant parameters $r_{O2\cdots Hbond}$ (1.93 Å) and $r_{Ow\cdots H11}$ (2.78 Å) are in agreement with the values for strong O···H−O and weak O···H−C[31] hydrogen bonds, respectively.

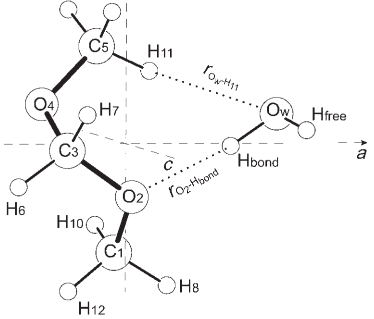

Figure 3. Sketch of dimethoxymethane–water with the principal axes and the hydrogen-bond parameters.

Conclusion

The configuration of the global minimum of the DMM–W complex has been determined from the analysis of the PJ-AMMW and FT-MW spectra of several isotopologues. The water moiety is linked in an asymmetric way to DMM, forming both strong O···H−O and weak O···H−C hydrogen bonds. The barriers to internal rotation of the two methyl groups (V_3(Me1) = 6.83(8) and V_3(Me2) = 6.19(8) kJ mol^{-1}), are similar to the value for the bare DMM molecule (6.62(8) kJ mol^{-1}).[20] Surprisingly, the V_3 value for the methyl group (Me1 of Figure 1), which interacts with the water molecule, is even closer to that of bare DMM. An explanation for the lowering of V_3(Me2) with respect to V_3(DMM) could be a weakening of the corresponding C−O bond upon formation of the hydrogen bond.

In contrast to most of the previously investigated ether–water complexes, the O−H···O linkage appears to be nearly linear.[9–12] The experimental value of the angle $\sphericalangle$O-H···O, 171°, coincides with the theoretical value (see Table 4).

Table 4. r_0 hydrogen-bond parameters of DMM···H_2O (see Figure 2).

	r_0	MP2/6–311++G**
r_{O2-Ow} [Å]	2.887 (9)[a]	2.816
$\sphericalangle O_wO_2C_3$ [°]	113.1(0.4)[a]	115
$\sphericalangle O_wO_2{-}C_3O_4$ [°]	79(1)[a]	78
$\sphericalangle H_{free}O_w{-}H_{bond}\cdots O_2$ [°]	156(4)[a]	167
$r_{Ow\cdots H11}$ [Å]	2.78[b]	2.744
$r_{O2\cdots Hbond}$ [Å]	1.93[b]	1.855
$\sphericalangle O_wH_{bond}\cdots O_2$ [°]	171[b]	171

[a] Fitted parameters; errors expressed in units of the last digit. [b] Derived parameters.

As for the lack of detection of the relatively stable conformer *E*, we presume that it is due to relaxation to the most stable conformer during adiabatic expansion.[32]

Experimental Section

A commercial sample of DMM, supplied by Aldrich, was used without further purification. Molecular clusters were generated in a supersonic expansion, under conditions optimized for 1:1 cluster formation. Two different experimental set-ups were used, as described below.

Pulsed-jet absorption millimeter wave (PJ-AMMW) spectroscopy: The Stark modulated pulsed jet absorption millimeter-wave spectrometer has already been described elsewhere.[33,34] The complex was formed by flowing DMM at 5% in argon at a pressure of approximately 0.8 bar over water at room temperature, and expanding the mixture through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.2 mm, to 2×10^{-3} mbar. An estimated "rotational" temperature of about 10 K was reached. The accuracy of the frequency measurements was about 50 kHz.

Coaxially oriented beam-resonator arrangement FTMW (COBRA-FTMW) spectroscopy: The details of the COBRA-FTMW spectrometer,[35] which covers the range 6–18.5 GHz, have been described previously.[36] The complex was formed by means of the pulsed supersonic expansion of a gas mixture composed of approximately 1% DMM FMS in He at a total backing pressure of 2 bar, flowed over a water reservoir at room temperature. Molecular pulses of approximately 0.40 ms duration followed by a MW polarization pulse of 10–20 mW for the μ_a and μ_c type transitions were required, while pulses of 2–3 mW were sufficient to polarize the μ_b transitions. Pulse lengths of about 0.60 µs were found to be optimal. Frequencies were determined after Fourier transformation of the 8k data points time domain signal recorded with 40 ns sample intervals. The pulsed molecular beam was introduced parallel to the axis of the Fabry-Pérot resonator, and consequently each observed transition appeared as a Doppler doublet. The line frequency was determined as the arithmetic mean of the frequencies of the two Doppler components. The accuracy of frequency measurements is estimated to be between 2 and 5 kHz, depending on the splitting pattern.

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