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Weak, Improper, C−O···H−C Hydrogen Bonds in the Dimethyl Ether Dimer

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Abstract: The ground-state rotational spectrum of the dimethyl ether dimer, $(DME)_2$, has been studied by molecular beam Fourier transform microwave and free jet millimeter wave absorption spectroscopies. The molecular beam Fourier transform microwave spectra of the $(DME\text{-}d_6)_2$, $(DME\text{-}^{13}C)_2$, $(DME\text{-}d_6)\cdots(DME)$, $(DME\text{-}^{13}C)\cdots(DME)$, and $(DME)\cdots(DME\text{-}^{13}C)$ isotopomers have also been assigned. The rotational parameters have been interpreted in terms of a C_s geometry with the two monomers bound by three weak C−H···O hydrogen bonds, each with an average interaction energy of about 1.9 kJ/mol. The experimental data combined with high-level ab initio calculations show this kind of interaction to be *improper*, blue-shifted hydrogen bonding, with an average shortening of the C−H bonds involved in the hydrogen bonding of 0.0014 Å. The length of the C−H···O hydrogen bonds, r(O···H), is in the range 2.52−2.59 Å.

Introduction

Noncovalent interactions play an important role in solvation processes,[1] in supramolecular chemistry,[2] in tertiary structures of proteins,[3] and in atmospheric chemistry.[4] Among them the hydrogen bond (H-Bond) represents a key interaction, generally involving higher interaction energies than, for example, electrostatic, dispersion, and hydrophobic interactions.[1,5]

Conventional H-bond interactions are of the X−H···Y type, with X and Y electronegative atoms such as oxygen and nitrogen. These H bonds are characterized by (i) a high interaction energy, in the range of 10−20 kJ/mol, and even more when resonance effects or charged particles are involved;[6] (ii) an increase of the X−H bond length and (iii) a decrease of the frequency of the X−H stretching (red shift) upon formation of the H-bond; and (iv) a transfer of a few percent of the electronic density from Y (the proton acceptor) to X−H (the proton donor). Another kind of H-Bond, named *improper-blue shifted* H-Bond, has been pointed out recently and investigated systematically by Hobza and co-workers.[7] It can be typically labeled as −WC−H···Z, where W and Z are electronegative groups: W (=O, N, Alg, π, ...) renders the adjacent H slightly acidic, while Z (=O, N, S, Alg, π, ...) acts as proton acceptor. This second type of H-bond is characterized by (i) a low interaction energy, in the range of 1−3 kJ/mol; (ii) a decrease of the C−H bond length and (iii) an increase of the frequency of the C−H stretching (blue shift) upon formation of the H-bond; and (iv) a transfer of a few millielectrons of the electronic density from Z (the proton acceptor) to W, the substituent inducing the acidic properties to the aliphatic H of the proton donor group. This H-bond interaction is weak, but it occurs very frequently and the cooperative effects are very important.

The configuration and the energy properties of such hydrogen bonding can be obtained from the rotationally resolved spectra, generally combined with free jet techniques.[8] The pure rotational spectrum of the difluoromethane dimer, with three C−F···H−C improper hydrogen bond interactions, has been reported recently.[9] Each C−F···H−C interaction was estimated to have an energy of about 2.2 kJ/mol. Each C−H bond involved in the H-bond had a decrease in the bond length of about 0.0015 Å and a blue shift of the C−H stretching in the range 13−21 cm^{-1}.

Dimethyl ether has C−H bonds adjacent to an electronegative atom, oxygen, and can offer both weak proton donors and proton acceptors. For these reasons it appeared a good candidate to form oligomers stabilized by improper blue shifted H-bonds. The conformation of the dimer is shown in Figure 1. We report here the results of Molecular Beams Fourier Transform Micro-

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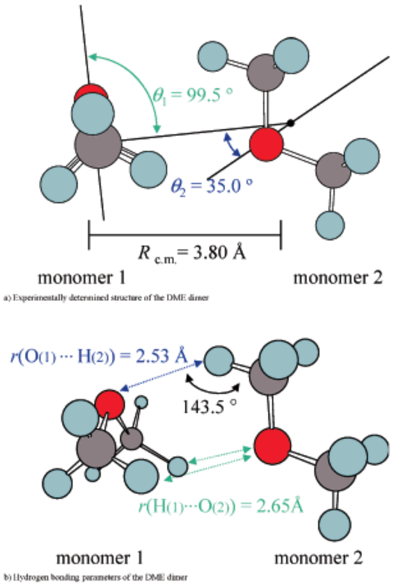

Figure 1. Configuration and experimental H-bond structural parameters of the DME dimer.

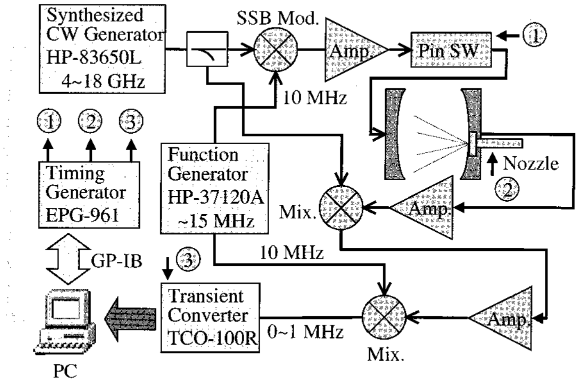

Figure 2. MB-MWFT spectrometer.

wave (MB-FTMW) and Free Jet Absorption Millimeterwave (FJ-AMM) spectroscopies, and relatively high level ab initio calculations.

Experimental Section

A commercial sample of DME (Aldrich) has been used without further purification.

The isotopically labeled dimethyl ethers, $^{13}CH_3O^{13}CH_3$ (DME-^{13}C) and CD_3OCD_3 (DME-d_6), were purchased from ISOTEC Inc.

Supersonic expansions have been used to generate molecular clusters, at conditions optimized for 1:1 cluster formation. Two different experimental setups have been used: a molecular beam Fourier transform microwave spectrometer (Shizuoka) and a millimeter-wave free jet absorption spectrometer (Bologna), which provided complementary results.

(a) MB-FTMW Spectroscopy. The FTMW spectrum was measured using a pulsed-beam Fabry-Perot-cavity Fourier transform microwave spectrometer of the Balle-Flygare type at Shizuoka University.[10] The vacuum chamber was a stainless steel cylinder with a diameter of 45 cm and a length of 80 cm. The chamber was evacuated with a 14 in. diffusion pump and a 600 m^3/h mechanical booster pump. The mirrors were aluminum with 26 cm diameter. A block diagram of the electronic components is shown in Figure 2.

The details of the spectrometer, which covers the range 6−18.5 GHz, are described elsewhere.[11] For the production of $(DME)_2$ Ar gas at a backing pressure of ∼2 bar was mixed with DME vapor at 20 mbar. This gas mixture was flowed through the solenoid valve (General Valve, Series 9) and expanded into the cavity (nozzle diameter 0.8 mm). The frequencies were determined after Fourier transformation of the 8 k data points time domain signal, recorded with 100 ns sample interval. The pulsed nozzle valve was mounted near the center of one of the mirrors in such a way that the supersonic beam propagates parallel to the resonator axis. Due to this setup, all lines appear as Doppler doublets. The line position was the arithmetic mean of both Doppler components.

(b) FJ-AMM Spectroscopy. The 60−78 GHz Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has been described elsewhere.[12,13] The dimer was formed expanding a mixture of ca. 10% in moles of DME in Argon (or Neon) at room temperature and at a pressure of ca. 0.8 bar to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm. An estimated "rotational" temperature of about 10−20 K has been reached. The accuracy of the frequency measurements was estimated to be 0.05 MHz.

The signal-to-noise ratio was about 10/1 for the most intense absorption lines.

Discussion

Rotational Spectra. The rotational spectra were assigned independently in Shizuoka and in Bologna.

In Shizuoka the FTMW spectrum of DME dimer was predicted by using the rotational constants obtained from ab initio calculation. Six isotopomers of the DME dimer were prepared by the proper mixing of three samples of DME, DME-^{13}C, and DME-d_6. In the search of the a-type transitions, very characteristic triplet lines, equally strong and equally separated, were found and were assigned as the $K = 0$ and 1 transitions for each J. The intensities of the c-type lines were, however, much weaker and more accumulation was needed for measurement. No b-type transition was observed. Only a-type transitions were assigned for the DME-d_6···DME and (DME-d_6)$_2$ isotopomers. The pairs of DME-^{13}C···DME-d_6 and DME-d_6···DME-^{13}C isotopomers were not tried and the DME-d_6···DME isotopomer has been observed; however, the DME ···DME-d_6 isotopomer could not be found, where the right (monomer1) and left DME (monomer2) represent those in and out of the symmetry plane of the complex as shown in Figure 1, respectively.

In Bologna trial rotational constants were calculated based on the geometries of isolated DME[14] and assuming O···H−C hydrogen bond parameters similar to those of F···H−C observed in difluoromethane dimer. Several a-type R branches were easily observed and about 80 a-type R lines measured for the normal isotopic species.

The measured rotational line frequencies (available as Supporting Information) of all isotopomers have been fitted within the I^r representation of Watson's "S" reduced Hamiltonian,[15]

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Table 1. Spectroscopic Constants of the DME Dimer[a]

	$(DME)_2$	$(DME\text{-}^{13}C_2)_2$	$(DME\text{-}^{13}C_2)$–(DME)	(DME)–$(DME\text{-}^{13}C_2)$	(DME-d_6)–(DME)	$(DME\text{-}d_6)_2$
A/MHz	5396.819(2)	5133.385(2)	5230.721(2)	5293.847(2)	4529.6(3)	4041.2(7)
B/MHz	1256.4886(2)	1201.1203(3)	1235.6418(3)	1221.7943(4)	1183.7659(3)	1061.8349(1)
C/MHz	1234.6834(2)	1179.3484(3)	1207.2242(3)	1206.4733(4)	1137.4773(3)	1039.9111(1)
D_J/kHz	2.1357(4)	1.927(3)	2.041(4)	2.018(3)	1.681(2)	1.2861(5)
D_{JK}/kHz	2.14(1)	2.12(2)	2.69(3)	1.60(3)	4.40(5)	2.06(2)
D_K/kHz	8.4(3)	9.8(4)	8.7(4)	13.8(7)	8.4[b]	8.4[b]
d_1/kHz	0.050(2)	0.040(3)	0.031(3)	0.058(3)	−0.006(2)	0.0256(6)
d_2/kHz	0.037(2)	0.049(1)	0.047(3)	0.045(2)	0.0374(9)	0.0370(4)
H_{JK}/Hz	−0.06(2)					
h_2/Hz	0.008(2)					
L_{JJK}/mHz	−0.05(2)					
$P_{bb}{}^c$/u Å^2	50.374	53.109	53.123	50.359	64.473	67.546

[a] Figures in parentheses are one standard deviation in units of the last digit. [b] Fixed at the value of the normal species. [c] $P_{bb} = {}^1/_2(I_a + I_c - I_b)$.

Table 2. Planar Moments of Inertia (in uÅ^2) and C···C Distances for the DME Dimer

	obsd		calcd[a]	
	P_{bb}	$\Delta P_{bb}{}^b$	P_{bb}	$\Delta P_{bb}{}^b$
$(DME)_2$	50.374		50.253	
$(DME\text{-}^{13}C_2)\cdot(DME)$	53.123	2.749		
$(DME)\cdot(DME\text{-}^{13}C_2)$	50.359			
$(DME\text{-}^{13}C_2)_2$	53.109	2.750		
$(DME)_2$	50.374		50.253	
$(DME\text{-}d_6)\cdot(DME)$	64.473	14.099	64.308	14.055
$(DME\text{-}d_6)_2$	67.546	3.073	67.528	3.220
r_s(C···C) = 2.341 Å[c] dimer				
r_s(C···C) = 2.334 Å monomer				

[a] Calculated assuming P_{bb}(dimer) = P_{aa}(monomer) + P_{cc}(monomer). [b] The ΔP_{bb} value given in a certain line is the difference between the P_{bb} value reported in the same line and the P_{bb} value given in the upper adjacent line. [c] For the DME unit out of symmetry plane of the complex.

producing the spectroscopic constants of Table 1. Besides rotational and quartic centrifugal distortion constants, some sextic centrifugal distortion parameters have been determined for the normal species. The high values of the centrifugal distortion parameters are related to the motions of the two monomers with respect to each other, as we will discuss later.

Conformation. The planar moments of inertia, P_{gg}, give the mass extension along the principal axes. The P_{bb} values, given at the bottom of Table 1, nearly coincide with the sums of P_{aa} and P_{cc} for the various isotopomers of isolated DME. This means that the extension of the dimer along the b axes corresponds to the contributions of four H atoms and two CH_3 groups, in agreement with the C_s conformation of Figure 1. From the ΔP_{cc} differences between $(DME)_2$ and DME···DME-^{13}C and between DME···DME-^{13}C and $(DME\text{-}^{13}C)_2$, the C···C distance of monomer 1 in the complex was calculated to be r_s(C···C) = 2.341 Å, which is very close to that in the isolated DME, r_s(C···C) = 2.334 Å.[14] For the deuterated isotopomers, the differences ΔP_{cc} =14.099 uÅ^2 between DME-d_6···DME and $(DME)_2$ and 3.073 uÅ^2 between DME-d_6···DME and $(DME\text{-}d_6)_2$ are close to the corresponding values of the isolated DME[14] 14.055 and 3.220 uÅ^2, respectively, as shown in Table 2.

Structure. From the experimental rotational constants of all measured isotopomers we obtained a further confirmation of the conformation. A plausible r_0 structure for the position of the two moieties with respect to each other, shown in Figure 1a, was obtained by the least-squares fits to the observed rotational constants of the six isotopomers, while keeping the geometries of DME as in the isolated molecules.[14] Three structural parameters $R_{c.m.}$, θ_1, and θ_2 were obtained to be 3.80 Å, 95.3°, and 35.3°, respectively, where $R_{c.m}$ is the distance between the centers of mass of the monomer, θ_1 and θ_2 are the angles between the connecting line of the centers of mass of the monomers and the C_{2v} axis of monomer 1 and monomer 2, respectively. More explicit H−Bond parameters are indicated in Figure 1b.

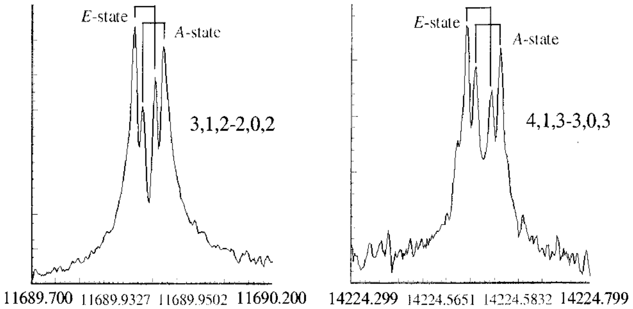

Figure 3. Hyperfine structure of rotational lines due to the "free" methyl group internal rotation.

Internal Rotation of the "Free" Methyl Group. Some transitions were split into two (A and E) component lines by the effects of the hindered rotation of the "free" methyl group (the one not involved in the H-bonds, see Figure 1). Figure 3 shows the experimental details of some of these transitions. The measured internal rotation splittings are collected in Table 3, together with the determined internal rotation parameters.[16] The V_3 barrier, 2.2 kcal/mol, is smaller than that of the monomer (2.6 kcal/mol).[14]

Dissociation Energy. The six translational and the six rotational degrees of freedom of the two monomers are reduced, upon formation of the dimer, to just the half, because six of them are converted to six low-energy vibrational modes. One of these motions can be considered as the stretching of the centers of mass of the two constituent molecules, while the remaining ones can be thought of as two bends and three internal rotations of one moiety with respect to the second one. For asymmetric top complexes in which the stretching coordinate is near-parallel to the inertial a-axis [condition satisfied for $(DME)_2$], the stretching force constant (k_s) can be estimated by approximating the complex to a molecule made of two rigid parts, by using the so-called pseudodiatomic approximation, expressed by the equation[17]

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Table 3. Splittings and Parameters Related to the Internal Rotation of the "Free" Methyl Group

(a) Internal Rotation Splitting in Dimethyl Ether Dimer

$J,K_a,K_c - J',K'_a,K'_c$	ν_A[a]	A–E splitting[b] obsd	calcd	O–C[c]
6, 2, 5−5, 2, 4	14944.6574	−0.0354	−0.0204	−0.0150
6, 2, 4−5, 2, 3	14947.7472	0.0372	0.0340	0.0032
7, 2, 6−6, 2, 5	17434.4205	−0.0198	−0.0043	−0.0155
7, 2, 5−6, 2, 4	17439.3664	0.0218	0.0200	0.0018
1, 1, 0−0, 0, 0	6653.2938	0.0134	0.0100	0.0034
2, 1, 1−1, 0, 1	9166.1975	0.0130	0.0113	0.0017
3, 1, 2−2, 0, 2	11689.9502	0.0175	0.0111	0.0064
4, 1, 3−3, 0, 3	14224.5832	0.0181	0.0100	0.0081
5, 1, 4−4, 0, 4	16770.2284	0.0183	0.0083	0.0100
6, 1, 5−5, 0, 5	19327.0808	0.0183	0.0059	0.0124
4, 0, 4−3, 1, 2	5746.2710	−0.0184	−0.0029	−0.0155
5, 0, 5−4, 1, 3	8191.7796	−0.0123	0.0007	−0.0130
7, 0, 7−6, 1, 5	13045.5599	−0.0159	0.0100	−0.0259
8, 0, 8−7, 1, 6	15452.8664	−0.0144	0.0158	−0.0302
5, 2, 4−5, 1, 4	12289.0896	0.0954	0.0982	−0.0028
6, 2, 5−6, 1, 5	12224.8249	0.0583	0.0741	−0.0158

(b) Internal Rotation Parameters

A_0/MHz	5396.8181(5)
B_0/MHz	1256.4897(1)
C_0/MHz	1234.6816(1)
F/MHz	161844[d]
ρ	0.03300[d]
s	64.65
V_3/kcal mol^{-1} [e]	2244 ± 15

[a] Transition frequency of A-state in MHz. [b] $\nu_A - \nu_E$ in MHz. [c] Observed − calculated. [d] Fixed. [e] Error does not include the uncertainty due to that in I_α.

$$k_s = 16\pi^4(\mu_D R_{CM})^2[4B_D^{\,4} + 4C_D^{\,4} - (B_D - C_D)^2(B_D + C_D)^2]/(hD_J) \quad (1)$$

where the suffix D stands for "Dimer". So μ_D, B_D, and C_D are the reduced mass and the B and C rotational constants of the dimer. R_{CM} and D_J are the distance between the centers of mass of the two subunits, and the first-order centrifugal distortion constant, respectively. The value $k_s = 4.7$ N/m, corresponding to a harmonic stretching frequency of 59 cm^{-1}, has been obtained. The dissociation energy (E_D) has been evaluated to be 5.7 kJ/mol by assuming a Lennard-Jones potential function, using the approximated equation[18]

$$E_D = (1/72)k_s R_{CM}^{\;2} \quad (2)$$

Such a dissociation energy corresponds to a binding energy of 1.9 kJ/mol for each of the three C−H⋯O−C linkages which stabilize the dimer. This value is very similar to that estimated for each of the three C−H⋯F−C bonds (2.2 kJ/mol) in the difluoromethane dimer.[9] The strength of this kind of H-Bond is much smaller than that of "normal" H-Bonds, such as O−H⋯O in complexes of water with ethers ($E_D = 22$ kJ/mol in dioxane−H_2O[19]), but the "cooperative effect" of the three weak C−H⋯O−C linkages makes the complex sufficiently stable for its detection with our techniques.

Table 3 compares the force constants, stretching vibration frequencies, and binding energies of the DME dimer to the values of some related dimers. All these parameters have been obtained from the centrifugal distortion constant D_J. The data for the formaldehyde dimer are from ref 20.

Table 4. Comparison of Force Constants, Stretching Vibration Frequencies, and Binding Energies of the DME Dimer to Those of Some Related Dimers (Values Calculated from D_J).

	k_s/N m^{-1}	ω_s/cm^{-1}	$R_{c.m.}$/Å	E_d/kJ mol^{-1}
$H_2C{=}O$ dimer[a]	6.2	84	3.05	4.8
difluoromethane dimer[b]	6.2	64	3.55	6.2
DME dimer[c]	4.7	59	3.80	5.7

[a] Reference 20. [b] Reference 8. [c] This work.

Table 5. H-Bond Parameters and Dissociation Energy (E_D) Obtained with Two Theoretical Methods Are Compared to the Experimental Values

parameter	obsd	MP2/6-311G**	MP2/6-311++G**
r(O(1)⋯H(2))/Å	2.53	2.44	2.52
r(H(1)⋯O(2))/Å	2.65	2.55	2.60
∠(O(1)⋯H(2)−C)/°	143.5	144.0	141.8
$-\Delta E$[a]/kJ mol^{-1}	5.7	2.5	9.6[b]

[a] $E_D = E(\text{dimer}) - 2E(\text{monomer})$. [b] Including a BSSE corrections of −6.7 kJ mol^{-1}.

Ab Initio Calculations. The experimental results have been confirmed by two different sets of ab initio calculations, at the MP2/6-311G(d,p) and MP2/6-311++G(d,p) levels, respectively. In both cases the potential energy minimum has been found and characterized by means of an analytic Hessian matrix calculation within the Gaussian98 package.[21] The two sets of H-Bond parameters and dissociation energies (E_D) are compared to the experimental values in Table 5. The value of the binding energy obtained with the second method has been corrected for basis set superposition error (BSSE), evaluated by means of the counterpoise procedure.[22]

The second method has been used to calculate also the geometry of isolated DME and the vibrational frequencies for either DME or DME dimer. By comparing the geometries and the frequencies of the C−H groups involved in the H-Bond, before and after the formation of the dimer, we can observe a blue shift of the corresponding stretching vibrations, and a shortening of the C−H bond lengths, as shown in Figure 4. This allows us to classify the interaction as improper, blue-shifting H-Bond, in agreement with the definitions of Hobza and collaborators.[7]

Some extra results, such as rotational constants and electric dipole moment components for DME and DME dimer, also obtained with the second method, are given in Table 6. The values of μ_a and μ_c are in agreement with the relative intensities of the observed lines.

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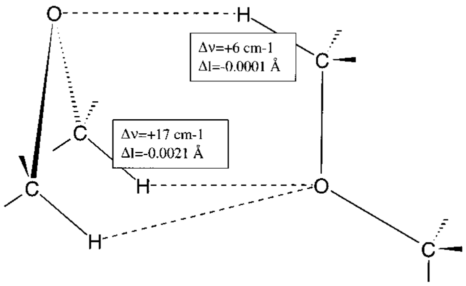

Figure 4. Shortening of the C−H bond lengths and blue shift of the corresponding stretching vibrations, upon formation of the dimer, of the C−H groups involved in the H bond.

Table 6. Ab Initio MP2/6-311++G** and Experimental Values of the Rotational Constants and Electric Dipole Moment Components of DME and DME Dimer

	monomer		dimer	
	exptl	ab initio	exptl	ab initio
A/MHz	38789.4	38475.6	5396.82	5409.6
B/MHz	10056.54	10183.5	1256.49	1284.4
C/MHz	8886.81	8971.57	1234.68	1265.1
μ_a/D	0.0	0.0		1.86
μ_b/D	1.302	1.65		0.0
μ_c/D	0.0	0.0		−0.63

Conclusions

This is, to our knowledge, the first report at a rotational resolution level on such a small triply hydrogen bonded dimer with three C−H···O−C improper, blue-shifting H-Bond interactions. Detailed information on the conformation, geometry, and dissociation energy have been obtained from the jet-cooled rotational spectrum. Ab initio calculations showed the hydrogen bond to have blue-shifting H-Bond features. This kind of interaction is not very strong, but very common, and for this reason is expected to play an important role in biology and in atmospheric chemistry. Biological systems display plenty of these interactions, generally neglected so far, with respect to "normal" H-Bonds, in evaluating tertiary structures. These interactions are becoming of relevant interest also in atmospheric chemistry because Freons are going to be replaced by oxygenated compounds; the formation of dimers can change considerably the energetics and the pathways of the degradation processes.

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Supporting Information Available: Table of experimental transition frequencies of six isotopic species of dimethyl ether dimer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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