Barrierless proton transfer across weak $\text{CH} \cdots \text{O}$ hydrogen bonds in dimethyl ether dimer

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We present a combined computational and threshold photoelectron photoion coincidence study of two isotopologues of dimethyl ether, $(\text{DME-h}_6)_n$ and $(\text{DME-d}_6)_n$ $n = 1$ and 2, in the 9–14 eV photon energy range. Multiple isomers of neutral dimethyl ether dimer were considered, all of which may be present, and exhibited varying $\text{C-H} \cdots \text{O}$ interactions. Results from electronic structure calculations predict that all of them undergo barrierless proton transfer upon photoionization to the ground electronic state of the cation. In fact, all neutral isomers were found to relax to the same radical cation structure. The lowest energy dissociative photoionization channel of the dimer leads to $\text{CH}_3\text{OHCH}_3^+$ by the loss of CH_2OCH_3 with a 0 K appearance energy of 9.71 ± 0.03 eV and 9.73 ± 0.03 eV for $(\text{DME-h}_6)_2$ and deuterated $(\text{DME-d}_6)_2$, respectively. The ground state threshold photoelectron spectrum band of the dimethyl ether dimer is broad and exhibits no vibrational structure. Dimerization results in a 350 meV decrease of the valence band appearance energy, a 140 meV decrease of the band maximum, thus an almost twofold increase in the ground state band width, compared with DME-d₆ monomer. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914456>]

I. INTRODUCTION

Proton transfer is important in biological, chemical, and atmospheric processes. Hydrogen bonds are known to facilitate inter- and intra-molecular proton transfer, in which the direction of the bond defines the reaction coordinate. The observation of protonated cluster fragments upon photoionization of molecular clusters is typically explained by fast intermolecular proton transfer occurring across hydrogen bonds.^{1,2} There have been a slew of gas-phase cluster studies on ionization induced proton transfer. Photoionization has been shown to produce protonated cluster fragments of several substances^{3–5} including water,^{6–8} methanol,^{9–11} ammonia,¹² and various hetero-clusters.^{13–17} Hydrogen atom and proton transfer are common gas-phase ion–molecule reactions of both polar and non-polar species.^{18–20} Thus, clusters weakly bound by van der Waals interactions are of particular interest for studying the gas phase ionization-induced chemistry, as they fill the gap between strongly H-bonded systems and molecules interacting upon collision.

There has been a long debate in the literature about what constitutes a hydrogen (H-) bond (see Refs. 21–25 and references therein). Pauli defined the H-bond as “...an atom of hydrogen...attracted by rather strong forces to two atoms, instead of only one, so that it can be considered to be acting as a bond between them.”²⁶ Traditionally, H-bonds are thought of as a H atom forming a bridge between two relatively elec-

tronegative atoms, $\text{X-H} \cdots \text{Y}$, where X and Y are typically N, O, or F atoms.²⁴ These “conventional” H-bonds are accompanied by an elongation of the covalent X–H bond and a red-shift in its vibrational frequency. Dimethyl ether (DME) has been reported to form unconventional “blue-shifted,”²⁷ sometimes referred to as improper, intermolecular H-bonds²⁸ with itself^{29,30} and other molecules.^{31,32} Although there is no fundamental distinction between a $\text{C-H} \cdots \text{O}$ interaction, e.g., those found in dimethyl ether dimer, and a “conventional” H-bond,^{23,25,28,33} the formation of “ $\text{C-H} \cdots \text{O}$ ” H-bonds can result in a contraction of the proton donating C–H bond and a blue-shift in the C–H vibrational frequency. The International Union of Pure and Applied Chemistry (IUPAC) definition of a hydrogen bond^{21,22} was broadened in 2011 to its current form and now includes some relatively weak $\text{C-H} \cdots \text{O}$ interactions.

Some of the authors have previously used velocity map photoelectron imaging of DME clusters and ultrafine aerosol particles³⁴ with a mean size distribution of >1000 monomer units per aggregate to study how condensation of neutral DME to form clusters affects the photoelectron spectra. A systematic lowering of the band maximum corresponding to the ground electronic 2B_1 state of DME cation by ~1 eV was observed with increasing particle size over the size range studied. Furthermore, a threefold broadening of the valence photoelectron band was observed. Mass spectra of DME clusters ionized with 10.1, 13.3, and 17.5 eV light all showed protonated cluster ion peaks.³⁵ A recent photoion mass spectrometry study by Golan *et al.*³⁶ has shown efficient proton transfer upon photoionization in 1,3-dimethyluracil dimer, a system similar to DME dimer in that it lacks “conventional”

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H-bonds. However, a relatively large barrier of 0.6 eV was calculated for the intermolecular proton transfer and attributed to a concerted reaction coordinate involving a significant rearrangement of both monomer units.

In this contribution, we discuss the barrierless proton transfer in and the fragmentation of DME- h_6 and DME- d_6 dimers upon photoionization by threshold photoelectron photoion coincidence (TPEPICO) spectroscopy in the 9–14 eV photon energy range. DME dimer is particularly interesting for the study of proton transfer because it exhibits only weak, “unconventional,” or arguably no hydrogen bonding in its neutral state.^{29,30,37} Nevertheless, single photon ionization of neutral DME clusters has been shown to produce nearly exclusively protonated cluster fragment ions.^{1,35} Calculations show that at least five DME dimer isomers with various C–H $\cdots$ O interactions may be present in the experiment and reveal that, for all studied isomers, proton transfer proceeds without a barrier in their respective lowest energy ionized states. To the best of our knowledge, this is the first observation of barrierless, intermolecular proton transfer in the absence of conventional hydrogen bonding. The effect of DME condensation on the photoelectron spectrum is also observed and compared to previous work on larger particles.

II. METHODS

A. Experimental

Imaging photoelectron photoion coincidence (iPEPICO) experiments were performed at the Vacuum Ultraviolet (VUV) beamline of the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland.^{38–40} DME- h_6 or DME- d_6 was seeded in Ar and expanded through a 150 μ m nozzle into high vacuum to form a continuous molecular beam. The DME- d_6 used in these experiments was synthesized⁴¹ at the ETHZ and found to be >99.8% isotopically pure. Methanol- d_4 ($\geq 99.8\%$ D substitution, Sigma–Aldrich) was used as a starting material. The nozzle diameter, the DME concentration, and the stagnation pressure were varied to achieve optimal dimer conditions, i.e., maximum dimer signal while larger clusters were suppressed. Molecular beam conditions were monitored by the dimer to protonated dimer peak area ratio ion spectrum recorded below the dimer dissociation energy (~ 9.8 eV photon energy). A relatively high sample concentration of 25% was found to be optimal at a stagnation pressure of 250 millibars. This produced a working pressure of $\sim 5 \times 10^{-4}$ millibars in the source chamber. The stagnation pressure had the greatest effect on the molecular beam: a 10 millibars lower backing pressure led to scarcely any cluster formation, and large clusters were formed in abundance at 10 millibars higher pressure. The molecular beam was skimmed by a 2 mm diameter skimmer at the entrance of the ionization chamber resulting in a background pressure of $1\text{--}4 \times 10^{-6}$ millibars during operation. In effusive experiments, room temperature DME was leaked into the ionization chamber yielding a similar background pressure. The sample was ionized by monochromatic VUV radiation with a resolution of better than 4 meV. Higher frequency light was suppressed with a differentially pumped gas filter using a Kr:Ne:Ar mixture. The photoelectrons and

photoions were extracted using a continuous, 120 V cm^{-1} field. Photoelectrons were velocity map imaged onto a fast delay-line detector with a better than 1 meV resolution in the center spot at zero kinetic energy. Their arrival times were also used as “start-signal” for the photoion time-of-flight analysis. Some non-zero kinetic energy electrons have no perpendicular momentum component to the flight axis and are also focused in the center spot. The resulting non-zero kinetic energy electron contamination of the central, threshold signal was subtracted to obtain threshold photoionization mass spectra.⁴² The smooth, 5 cm long 1st ion extraction field results in ion residence times on the order of several μ s. Metastable ions dissociating during this time are detected between the fragment and the parent ion time-of-flight and yield a quasi-exponentially decaying daughter ion peak characteristic of dissociation rate constants in the $10^4 < k < 10^7 \text{ s}^{-1}$ range. Data were collected in the photon energy range of 9–14 eV using step sizes between 5 and 50 meV and integration times between 180 and 360 s. The detection of photoions in delayed coincidence with zero kinetic energy photoelectrons allows us to control the energy balance of (dissociative) photoionization, because the excess photon energy above the adiabatic ionization energy (AIE) is deposited in the photoion as internal energy.

Threshold photoionization mass spectra collected using photon energies of 9.740 and 10.180 eV are shown in Figure 1. The lower photon energy in Figure 1, 9.740 eV, was chosen because it is near the band maximum of the intact dimer signal and below the appearance energy (AE) of the deuterated monomer. The higher photon energy, 10.180 eV, was chosen because it is above the point where all photoionized dimers dissociate into deuterated monomers. Based on data at these two photon energies, we estimate the dimer content in the molecular beam to be about 1%–2% that of the monomer. We were routinely able to achieve conditions where no trimer was detectable in the mass spectrum. However, there was always a detectable amount of protonated or deuterated dimer, $(\text{CH}_3\text{OCH}_3)_2\text{H}^+$ or $(\text{CD}_3\text{OCD}_3)_2\text{D}^+$, which arose from fragmentation of larger neutral clusters, $n > 2$, in the molecular

FIG. 1. Threshold photoionization mass spectra of DME- d_6 . The molecular beam sample contained nearly exclusively monomers and dimers at photon energies of (a) 9.740 eV which is below the dissociation energy of the dimer and (b) 10.180 eV where all ionized dimers dissociate into protonated or deuterated monomer (shown as $(\text{CD}_3)_2\text{OD}^+$ in inset). The TPEPICO signal is plotted in counts per second (counts/s).

beam, and could typically be suppressed to $<0.3\%$ of the monomer signal by optimizing the molecular beam conditions.

In the mass spectrum of DME- h_6 , the main ^{13}C isotope peak of the intact DME monomer ion has an intensity that is 2.2% that of the DME- h_6^+ signal having two ^{12}C atoms and coincides with the main peak of the protonated monomer (fragment ion from dimer dissociation) at our experimental mass resolution of 150. For this reason, we performed most experiments with DME- d_6 . Because of the $m/z = 2$ difference between $(\text{DME-}d_6)_n^+$ and $(\text{DME-}d_6)_n\text{D}^+$, the ^{13}C peak of the intact DME and that of the deuterated species with two ^{12}C atoms are baseline separated in the time-of-flight mass spectrum of DME- d_6 . This makes the acquisition of photoion mass selected threshold-photoelectron spectra (TPES) straightforward. Furthermore, if proton transfer were rate determining in the dissociative photoionization process, quantum tunneling rates would be quenched in the deuterated dimer. Thus, by accurately measuring the effective dissociative photoionization barrier in both the light and deuterated dimers and comparing the shift with the zero-point energy effect, we can gain insight into the proton transfer dynamics.

B. Computational

Geometry optimization of the neutral DME monomer and the dimers was performed with resolution of the identity Møller-Plesset second order perturbation theory (RI-MP2) and density functional theory (DFT) methods using the cc-pVTZ basis set in Q-Chem.^{43,44} A long-range and dispersion-corrected $\omega\text{B97X-D}$ functional⁴⁵ was employed for all DFT calculations. RI-MP2 and $\omega\text{B97X-D}$ geometry optimizations resulted in nearly identical equilibrium configurations. For the two approaches, relative energies between the dimer isomers differ by less than $0.5 \text{ kcal mol}^{-1}$. All the data reported here refer to $\omega\text{B97X-D}$ structures unless stated otherwise. Geometries of the cations, proton-transferred structures, and neutral radicals were optimized at the same $\omega\text{B97X-D/cc-pVTZ}$ level. The true minimum character of all stationary points was verified by computing the Hessian matrix, for which no imaginary frequencies were observed. The coordinates of the optimized geometries are given in the supplementary material.⁴⁶

Vertical ionization potentials were computed using the equation-of-motion coupled-cluster approach for ionization potentials, EOM-IP-CCSD,^{47,48} with the aug-cc-pVTZ basis set. To quantify the dimer isomerization free energies, as well as adiabatic ionization energies and reaction product appearance energies, $\omega\text{B97X-D/cc-pVTZ}$ harmonic vibrational frequencies were used within the ideal-gas rigid-rotor harmonic-oscillator (IG-RR-HO) approximation.

To characterize the energetics of the proton transfer in ionized DME dimers, we performed a series of constrained geometry optimizations with fixed C–H bond length at the $\omega\text{B97X-D/6-311+G(d,p)}$ level of theory. Cation radical geometry optimization starting from the equilibrium geometries of all dimer isomers resulted in a proton-transferred structure, which is consistent with barrierless proton transfer in the ionized state.

FIG. 2. Photoion mass selected threshold photoelectron spectra of the DME- d_6 monomer and its major fragment ions. TPEPICO signal is plotted in counts/s.

The Gaussian09 package⁴⁹ was used to obtain vibrational frequencies and rotational constants of the neutral dimer conformer 1, the parent ion, and the dissociation products at the MP2/cc-pVTZ level of theory. These quantities were then used to construct the statistical model described below to fit the experimental breakdown diagram and dissociation rates. In addition, we also carried out complete basis set—atomic pair natural orbital (CBS-APNO) composite method calculations to obtain more reliable energetics for the dissociative photoionization process.⁵⁰

III. RESULTS AND DISCUSSION

A. Threshold photoelectron spectrum of DME monomer

The light^{34,51–55} and partially deuterated⁵⁶ dimethyl ether isotopologues have been the subject of numerous photoelectron spectroscopic as well as coincidence studies. We have measured the photoion mass selected (ms-)TPES of DME- h_6 and DME- d_6 monomers along with their ion fragments, but will focus on DME- d_6 , shown in Figure 2. Table I lists the experimental AE and band maxima, as well as calculated values of the AIE and vertical ionization energy (VIE), respectively, for the low-lying electronic states of DME – d_6^+ . The reported AE values are defined as the photon energy where the TPE signal is twice the noise level, and reported error bars are an estimate of the uncertainty associated with the measurement.

TABLE I. Experimentally determined AE, band maxima, and full widths at half maximum (FWHMs) along with calculated AIE and VIEs for ionization of the valence orbital of the monomer DME- d_6 .

Ion state	Experiment			Calculation	
	AE/eV	Band maximum/eV	FWHM/eV	AIE/eV	VIE/eV
$\tilde{X}^2B_1$	9.78 ± 0.03	10.11 ± 0.04	0.3 ± 0.1	9.82	10.09
$\tilde{A}^2A_1$		11.94 ± 0.03	0.7 ± 0.1		11.93
$\tilde{B}^2B_2$		13.49 ± 0.03			13.69

TABLE II. Experimentally determined AE, band maximum, and FWHM for the three lowest-lying valence photoion states of (DME-d₆)₂.

Ion state ^a	AE/eV	Band maximum/eV	FWHM/eV
$\tilde{X}^2B_1$	9.42 ± 0.07	9.97 ± 0.03	0.6 ± 0.1
$\tilde{A}^2A_1$		11.75 ± 0.03	1.0 ± 0.2
$\tilde{B}^2B_2$		13.31 ± 0.03	

^aThe corresponding monomer ion states are used as labels.

As shown in the ms-TPES of the DME-d₆ monomer in Figure 2, the fragment ions C₂D₅O⁺, $m/z = 50$, CD₃O⁺, $m/z = 34$, and CDO⁺, $m/z = 30$ appear at photon energies of 11.08, 11.66, and 12.87 eV, respectively. These energies are in qualitative agreement with the onsets reported for light DME in the TPEPICO study by Butler *et al.*⁵² Since there is no experimental TPES of DME-d₆ available in the literature, we will use our measured monomer TPE spectrum to determine ionization energy shifts and broadenings associated with dimerization of DME.

B. DME dimer

1. Threshold photoelectron spectrum of the DME-d₆ dimer

The ms-TPES of intact (DME-d₆)₂⁺ dimer ($m/z = 104$) and its sole fragment ion, deuterated DME-d₆, (DME-d₆)D⁺ ($m/z = 54$) recorded at photon energies between 9.2 and 14.0 eV are shown in Figure 3. Since the deuterated monomer is found to be the only fragment ion of the dimer in this energy range and the molecular beam contained nearly exclusively monomers and dimers (no larger clusters contributing to ms-TPES signals), the TPES of the DME dimer corresponds to the sum of the two ms-TPES signals shown in Figure 3. The intact (DME-d₆)₂⁺ dimer and (DME-d₆)D⁺ signals appear at $h\nu = 9.42 \pm 0.07$ eV and 9.60 ± 0.02 eV, respectively. The intact dimer cation dissociates completely into deuterated monomer upon threshold photoionization at photon energies above ~ 9.85 eV. The experimentally determined AE, band maximum, and FWHM for the three energetically lowest-lying valence photoion states of the fully deuterated DME dimer are given in Table II.

FIG. 3. Photoion mass selected threshold photoelectron spectra of (DME-d₆)₂⁺ dimer (solid blue circles) and its fragment ion (DME-d₆)D⁺ (open red circles). The data were collected under dimer conditions. TPEPICO signal is plotted in counts/s.

FIG. 4. Optimized structures of the five lowest lying isomers (labeled isomer 1-5) of DME dimer and the optimized dimer cation structure. The colors white, gray, and red correspond to hydrogen, carbon, and oxygen atoms, respectively. Optimized geometries are given in the supplementary material.⁴⁶

2. DME dimer isomers

Five neutral DME dimer isomers were found by Hermida-Ramon and Rios⁵⁷ with energy differences between them so small that the inclusion of the entropic and thermal factors changes their relative stability. We used these five isomers as starting structures in the present work and kept the numbering of the isomers for consistency. Figure 4 shows optimized geometries for the five DME dimer isomers studied, as well as the optimized geometries of DME₂⁺, the relative energies of the dimer isomers are listed in Table III.

Considering the Gibbs free energy of the isomerization reaction at 100 K, $\Delta_r G_{100K}$, all five structures lie within 0.8 kcal mol⁻¹. Due to the small differences in energy and their reordering with changes in temperature, we assume that at least these five dimer isomers, and possibly more, are populated in our experiment. Furthermore, these structures may span a rather anharmonic and interconnected potential energy surface, on which the isomers may interconvert below the barrier to dissociation into two separated monomers. All isomers were considered when comparing the experimental TPES and calculation results. The most stable 0 K structure, dimer isomer 1, is used as reference in 0 K binding energy and dissociative photoionization energy derivations.

TABLE III. Relative energies for DME dimer isomers. Thermodynamic quantities were computed in the rigid-rotor and harmonic-oscillator approximation using ω B97X-D/cc-pVTZ frequencies and geometries. CCSD/aug-cc-pVTZ energies were used.

	DME dimer isomer				
	1 (C _s)	2 (C _{2h})	3 (C _{2v})	4 (C _s)	5 (C _{2h})
$\Delta_r E/\text{kcal mol}^{-1}$	0	0.48	1.42	1.48	0.08
$\Delta_r H^\circ/\text{kcal mol}^{-1}$	0	-0.06	-0.17	-0.22	-0.07
$\Delta_r S^\circ/\text{cal mol}^{-1} \text{K}^{-1}$	0	5.58	7.70	5.26	-2.63
$\Delta_r G_{298K}/\text{kcal mol}^{-1}$	0	-1.24	-1.04	-0.31	0.79
$\Delta_r G_{100K}/\text{kcal mol}^{-1}$	0	-0.14	0.48	0.73	0.27

The five dimer isomers exhibit various C–H···O interactions, nearly all of which produce a slight “blue-shift” of the donating C–H stretch frequency and are not accompanied by an increase the proton donating C–H bond length with respect to the isolated gas phase monomer. H-bond strength has been connected to a shift of the proton from the donating toward the accepting atom,⁵⁸ with the strongest bonds having the proton near the center of the H-bridge. In the studied dimer isomers, the C–H distance is always around 1.1 Å, while the H···O distances and C–H···O angles in the five isomer are between 2.4 and 2.9 Å and 88 and 153°. The H···O distances and C–H···O angles found for the DME dimer tend to be longer and narrower, respectively, than those found for several other intermolecular C–H···O interactions (see Ref. 58 and references therein). The atomic distances and bond angles associated with the C–H···O interactions found for the neutral DME dimers are at the limit of what one could call a H-bond, and arguably the van der Waals forces binding these clusters are not H-bonds even in the current, broad IUPAC definition of the term.

Vertical IEs for the five neutral DME dimer isomers are listed in Table IV. The three lowest-lying monomer valence electronic states of the cation are split upon dimerization and are denoted by the subscripts *a* and *b* in Table IV. In the first approximation, the splitting is due to different orbital energies of the analogous orbitals on each of the monomer units of the ionic dimer complex. The calculated molecular orbitals corresponding to the VIEs listed in Table IV are shown in Figure S1 in the supplementary material.⁴⁶ The H-donating monomer unit had a lower IE than the H-accepting one in all studies isomers, except the high symmetry cases of isomer 2 and 5 where the two monomer units composing the dimer complex were both H-donating and accepting. The lowest IE of the dimer complex corresponded to an electron hole residing on the lone pair orbital of the O atom of the H-donating monomer unit.

3. Ionization-induced proton transfer

Vertical ionization to the lowest lying ionic state of each DME dimer isomer results in an electron coupled proton transfer to produce the radical cation dimer complex. In all DME neutral dimer structures studied, proton transfer was found to proceed without a barrier upon vertical ionization to the electronic ground state of the dimer isomer cations.

TABLE IV. VIEs of the five DME dimer isomers shown in Figure 4 computed with EOM-IP-CCSD/aug-cc-pVTZ. The C_{2v} symmetry is lost in the dimer isomers, and the three ion states (labeled 1–3) are each split (denoted with subscripts *a* and *b*).

VIE/eV state	DME dimer isomer				
	1 (C_s)	2 (C_{2h})	3 (C_{2v})	4 (C_s)	5 (C_{2h})
1 _a	9.72	9.89	9.65	9.86	9.81
1 _b	10.03	9.91	10.21	10.13	9.97
2 _a	11.59	11.42	11.45	11.70	11.69
2 _b	11.91	11.94	12.06	11.98	11.84
3 _a	13.36	13.35	13.28	13.41	13.45
3 _b		13.48	13.80		13.48

FIG. 5. Constrained geometry optimization of the DME dimer cation upon ionization of DME dimer isomer 1. The Franck–Condon point is defined as the energy required to produce an ion with the same geometry as the neutral dimer and is used as a reference. Relative energies (ΔE) are plotted as a function of C–H bond length, R_{C-H} , in the hydrogen donating bond (top). For each data point, the C–H bond length is fixed and the geometry of the rest of the dimer complex is allowed to relax. The singly occupied $\omega B97X-D/6-311+G(d,p)$ orbital for a representative point along the proton transfer is also shown. Partial charge distributions between (Q_D) donor and acceptor (Q_A) excluding partial charge on H-atom as well as the corresponding partial spin densities (SD_D and SD_A for donor and acceptor, respectively) are given in the lower panel.

Furthermore, all dimer isomers relaxed to the same proton transferred, radical cation geometry. As an example, the top panel of Figure 5 shows the energy profile corresponding to a constrained geometry optimization of the DME dimer cation (beginning with the neutral isomer 1 geometry, $\Delta E = 0$) as a function of C–H bond length. Vertical ionization brings the system in its neutral geometry to the cation potential energy surface, noted as the Franck–Condon (FC) point. The H-donating C–H bond has a length of 1.096 Å in isomer 1 of the neutral DME dimer in Figure 5. When the H-donating C–H bond is fixed at 1.096 Å and the rest of the dimer cation complex is allowed to relax, a geometry with 0.47 eV lower energy (ΔE) is found. Next, the donating C–H bond length is increased stepwise toward the H-accepting O atom on the neighboring DME monomer. The geometry of the rest of the dimer complex is allowed to relax after each step of the C–H bond length. The data point at $R = 1.651$ Å in Figure 5 corresponds to the minimum energy geometry of the DME dimer cation with a fully transferred proton. In the optimized proton transferred geometry, the C–H distance is 1.651 Å, the OH distance is 1.062 Å, and the O–H–C angle is 172.0° (see Figure 4 for structure).

Hydrogen atom transfer can be ruled out based on charge and spin density distribution analysis on the proton-donating and proton-accepting monomers (lower panel of Figure 5). The partial charge (denoted Q in Figure 5) migrates from the donating monomer unit (Q_D) to the accepting monomer unit (Q_A) as the C–H bond is stepped from the optimal neutral monomer distance to the optimal distance for the cation structure. Furthermore, more than 80% of the unpaired spin density (denoted SD in Figure 5) resides on the proton-donating fragment for a final proton-transferred structure. Moreover, it monotonically increases from 0.71 to 0.85 upon

elongation of the C–H bond, which is consistent with proton transfer but not with hydrogen transfer.

Note that despite differences in relative orientation of the monomer units in the neutral dimer isomers, ionization leads to the same proton-transferred, radical cation structure. This means that in contrast to strongly H-bonded dimers, in which H-bonds guide the proton-transfer and no significant rearrangement of monomers is observed,⁵⁹ in weakly bound dimers, the reaction coordinate can be more complex and involve significant motion of the monomer units. Nevertheless, the DME dimer is an example of a weakly bound system that undergoes barrierless proton transfer upon photoionization.

4. Dissociative ionization in DME dimer

We consider the following ionization-induced reaction pathways in the DME dimer:

Table V summarizes the calculated AIEs and the 0 K reaction product appearance energies, AE_0 , for the product ions of pathways (1) through (4) for both light and fully deuterated samples. The AE_0 of $\text{CH}_2\text{CH}_2\text{OH}_2^{+\cdot}$ from the dissociative DME dimer ionization is included in the table as it is a lower energy structural isomer of ionized DME monomer.

For the five neutral isomers of DME dimer, the calculated AIEs of intact $(\text{DME-d}_6)_2^+$ (see reaction (1)) are around 8.5–8.6 eV, in contrast with the experimentally observed appearance energy of 9.42 ± 0.07 eV. This discrepancy is due to a large geometry change upon ionization and consequent poor Franck–Condon factor for the 0–0 transition. All studied neutral isomers relax to the same ionic structure, which involves an intermolecular/intracluster proton transfer with a significant change in relative position of the two monomer units. This finding is in line with previous studies on dimers bound by conventional hydrogen bonds, which also undergo barrierless proton transfer upon ionization.² The binding energy of the ionized DME dimer complex, $AE_0[(\text{DME})\text{D}^+] - \text{AIE}[(\text{DME})_2^+]$, is ~ 1.2 eV or 28 kcal mol^{−1} according to our

calculations. This is a notable increase in binding energy from the neutral DME dimer complex, which we propose is on the order of 2.9 kcal mol^{−1} (see Sec. III B 5), and even larger if we consider the results of Tatamitani *et al.*, who used spectroscopic constants obtained from rotational spectra to determine a binding energy of 1.4 kcal mol^{−1} for neutral DME_2 .²⁹

Reaction (2) yields $\text{DME}(\text{H})^+$ after ionization induced proton transfer and subsequent dissociation of DME dimer. For the five neutral isomers of DME dimer, calculated AE_0 s of $\text{DME}(\text{H})^+$ and $\text{DME}(\text{D})^+$ are between 9.72 and 9.76 eV (see Table V). The AE_0 found from modeling the experimental data is 9.71 ± 0.03 eV for DME-h_6 dimers and 9.73 ± 0.03 for DME-d_6 dimers (see modeling discussion below). Above the AE of $\text{DME}(\text{H})^+$, we observe a decrease in the DME_2^+ signal and a corresponding increase in the $\text{DME}(\text{H})^+$ or $\text{DME}(\text{D})^+$ signal. Reaction (2) is the dominant dissociation pathway upon photoionization of the DME_2 .

Reaction (3) yields intact DME^+ from the dissociation of DME_2^+ without a proton transfer. Because the binding energy in the van der Waals bound neutral dimer is small, the calculated AE_0 s, between 9.83 and 9.86 eV for the five isomers, are quite close to the AIE of DME monomer, 9.82 eV. Since the dimer abundance in the molecular beam is only 1%–2% of the monomer, it is difficult to ascertain whether reaction pathway (3) takes place. However, because of the large force along the proton transfer coordinate at the Franck–Condon point and the more stable products of pathway (2), pathway (3) is unlikely to be significant. Furthermore, the DME^+ ms-TPES has not been added to the dimer TPES (as can be seen below in Figure 7). Still, there appears to be no missing component or sudden decay in the spectrum, which suggests that pathway (3) is not significant.

Reaction (4) results in a structural isomer of the DME cation that is lower in energy than the ionized DME monomer. In order to form $\text{CH}_2\text{CH}_2\text{OH}_2^{+\cdot}$ in our experiment, $(\text{DME})_2$ would need to be ionized, dissociate without undergoing proton transfer and the charge carrying monomer unit would need to isomerize on the sub-microsecond timescale that the ionized molecules spend in the extraction field. The calculated AE_0 of $\text{CH}_2\text{CH}_2\text{OH}_2^{+\cdot}$ from dimer dissociation is 9.53 eV, while the measured AE of the monomer cation is 9.78 ± 0.03 eV with and without dimers present in the molecular beam. With dimers present in the molecular beam, there is no monomer m/z signal below the AE of the monomer, 9.78 eV. We, therefore, conclude that the barriers must be too high for isomerization of the heavy-atom skeleton in the photon energy range studied. Reaction (4) does not occur in the experiment to any appreciable degree.

TABLE V. Calculated AIEs and 0 K dissociative ionization energies at (AE_0) for the ion products of dimer dissociation computed with EOM-IP-CCSD/aug-cc-pVTZ// ω B97X-D/cc-pVTZ. Basis set superposition error (BSSE) and zero point energy (ZPE) corrections have been included.

Calculated AIE or AE_0 /eV	DME dimer isomer				
	1	2	3	4	5
$(\text{DME-d}_6)_2^+$	8.57	8.58	8.56	8.56	8.56
$(\text{DME-d}_6)\text{D}^+$	9.75	9.76	9.73	9.72	9.74
DME-d_6^+	9.86	9.86	9.84	9.83	9.85
$\text{CD}_2\text{CD}_2\text{OD}_2^{+\cdot}$	9.53				
$(\text{DME-h}_6)_2^+$	8.68	8.69	8.65	8.65	8.67
$(\text{DME-h}_6)\text{H}^+$	9.76	9.76	9.72	9.73	9.74
DME-h_6^+	9.84	9.84	9.81	9.81	9.82
$\text{CH}_2\text{CH}_2\text{OH}_2^{+\cdot}$	9.52				

5. Modeling of dimer dissociation

As discussed above, metastable parent ions can lead to asymmetrically broadened daughter ion peak shapes, which are characteristic of the dissociation rate constant. The dissociative photoionization data can be concisely plotted in the breakdown diagram and daughter ion peak center-of-gravity (CoG) plot as shown in Figure 6. In the TPEPICO breakdown diagram, fractional ion abundances of DME dimer and its fragment ion, where the sum of the dimer and fragment

FIG. 6. (a) DME dimer breakdown diagram showing how the intact dimer is consumed by dissociative photoionization to yield the protonated monomer. The traces in (a) correspond to modeling results of the breakdown diagram for DME-h₆ (blue) and DME-d₆ (red) with corresponding experimental data for the fractional ion abundance of (DME-h₆)₂⁺ (solid blue line), (CH₃)₂OH⁺ (dashed blue line), (DME-h₆)₂⁺ (solid red line), and (CD₃)₂OD⁺ (dashed red line). (b) The CoG plot of the daughter ion is a measure of the dissociation rate constant and is used to derive the 0 K appearance energy, AE_0 . The experimental data points for (CH₃)₂OH⁺ are shown as blue x's and for (CD₃)₂OD⁺ as red +s. The modeling results of the mass spectral peak CoG are shown as solid traces in (b).

ion signals is normalized, are plotted as a function of photon energy. Slow dissociations also take place during those few μ s while the parent ion crosses the acceleration region. The resulting ion time-of-flight will be between that of a promptly formed daughter ion and that of the parent ion. One way to quantify the dissociation rates is by calculating the CoG of the daughter ion peak. The CoG of the daughter ion will be high for a slow dissociation. Since the parent ion internal energy increases with the photon energy (the dissociation will become increasingly prompt), the CoG of the daughter ion peak will converge to the flight time corresponding to the daughter ion m/z as the photon energy increases. The CoG

FIG. 7. Threshold photoelectron spectra of the sum of DME-d₆ monomer and its major fragment ions (top panel) and the sum of DME-d₆ dimer and its major fragment ion (bottom panel). The dashed vertical lines in bottom panels indicate calculated VIEs. See Tables I and IV for the VIEs of the monomer and dimer, respectively. See Figures 2 and 3 for the individual TPES spectra that were summed to in order to produce the “monomer” and “dimer” spectra presented here.

curves of (CH₃)₂OH⁺ and (CD₃)₂OD⁺ are plotted as a function of photon energy in the lower panel of Figure 6. At photon energies for which the parent is no longer metastable, the daughter ion peak in the mass spectrum is symmetric and centered at its characteristic TOF.

If the dissociation is fast, the shape of the breakdown curve corresponds to the cumulative internal energy distribution of the sample: all parent ions with sufficient energy to dissociate will do so, and the parent ion fractional abundance reaches zero at the dissociative photoionization threshold, in other words, at the 0 K appearance energy AE_0 . Modeling of the dissociation rate curve is essential to derive accurate energetics in metastable dissociations when a given amount of excess energy, also referred to as kinetic shift, is required for the parent ion to dissociate within the time scale of the experiment, i.e., before the parent ion leaves the acceleration region of the mass spectrometer.⁶⁰ Modeling of CoG plots to obtain the unimolecular dissociation rate curve has been shown to be equivalent to peak shape analysis.^{60,61} In addition to the internal energy distribution of the neutral species, the density of states of the dissociating species and the number of states at the transition state are used to calculate rates in a statistical model. As suggested earlier for dissociations taking place without a reverse barrier, we used the simplified statistical adiabatic channel model (SSACM) approach.⁶² SSACM can be thought of as a scaled phase space theory approach, in which the number of states of the transitional modes is calculated assuming unhindered translations and rotations along them. The number of states function is then scaled with an energy-dependent “rigidity” factor, $f_{\text{rigid}} = e^{-E/c}$, where E is the energy above the barrier and c is the rigidity constant.⁶⁰ In the model, the rigidity constant and AE_0 are the two variable parameters which are fitted to reproduce the experimental breakdown diagram and rate information simultaneously.

In their energetically lowest lying dissociative photoionization process, DME dimer cations lose a CH₃OCH₂ neutral fragment and yield protonated DME, CH₃O(H)CH₃⁺. If the dissociation was fast with no kinetic shift, the shift in the breakdown diagram would be equal to the AE_0 difference between the light and deuterated dimer, which in turn should be determined by the zero-point energy difference, which in this case is less than 20 meV. However, there is a 60 meV shift in the 50% crossover energy in the breakdown diagrams of the two isotopologues of DME, from 9.715 to 9.775 eV, upon deuteration. Analysis of the experimental rate curve is essential to determine the reason for this discrepancy. Deuteration may broaden the internal energy distribution and by leading to a looser parent ion and fragments, it can also affect the dissociation rates. On the other hand, the relatively large shift observed in the crossover energy can also be indicative of proton/deuteron transfer kinetics governing dissociative photoionization instead of the product energetics. By modeling the breakdown diagrams together with the CoG plots, we can establish a DME-h₆ dimer dissociative photoionization threshold of 9.71 ± 0.03 eV and a DME-d₆ dimer onset of 9.73 ± 0.03 eV. The model is based on a Boltzmann-type internal energy distribution at a phenomenological temperature of 110 K for both light and deuterated DME dimers based on the calculated rotational

constants and harmonic vibrational frequencies of the light and deuterated dimer isomer 1. While the rotational and vibrational degrees of freedom are cooled differently in a supersonic expansion, the good fit to the experimental data indicates that the average internal energy of $1.2 \text{ kcal mol}^{-1}$ or 53 meV and the shape of the overall internal energy distribution are reasonably reproduced by the model. On this basis, an AE_0 shift of only $20 \pm 15 \text{ meV}$ was found from modeling the experimental data, comparable to the calculated zero point energy shift of about $5 \pm 10 \text{ meV}$ depending on the level of theory used.

The breakdown curve shift can be rationalized in terms of the kinetic isotope effect, k_H/k_D , which converges to 7 at high energies in the model and is similar when calculated *ab initio*. The model rate curves can be found in Figure S2 of the supplementary material.⁴⁶ In rigid systems, the H/D kinetic isotope effects are related to activation energy differences because of zero-point energy shifts and quenched tunneling rates across the barrier in deuterated activated complexes. The DME cation, however, is a very floppy system with no barrier for proton/deuteron transfer. The large isotope effect is caused by the isotope dependence of vibrational frequencies and the corresponding densities of states.

The TPEPICO experiments yield the dissociative photoionization energies at 0 K, which corresponds to the lowest energy dimer at 0 K, isomer 1, yielding $(\text{DME} - \text{H})^+ + (\text{DME} + \text{H})^+$ from reaction (2). For the same process, the CBS-APNO composite method yielded a computed $AE_0 = 9.72 \text{ eV}$ for isomer 1 of the light DME dimer, in excellent agreement with the experimental AE_0 . The CBS-APNO calculated monomer adiabatic ionization energy of 10.00 eV also agrees well with the center of the 0–0 transition in the monomer TPES. Because of its good agreement with the observations of dissociative photoionization and the ionization energies, there is reason to believe that the third quantity calculated using CBS-APNO, namely, the binding energy of the neutral dimer isomer 1 at 0 K of $2.9 \text{ kcal mol}^{-1}$ is more accurate than the previously reported value of $1.4 \text{ kcal mol}^{-1}$.²⁹

C. Comparison of monomer and dimer photoelectron spectra

The TPE spectrum of the DME monomer and dimer, see Figure 7, shows a red shift and band broadening of the valence electronic bands upon formation of a dimer complex. The monomer spectrum (upper panel) in Figure 7 is obtained from the sum of the intact DME-d_6^+ ms-TPES and that of fragments attributed to its dissociation (see Figure 2). The dimer spectrum (lower panel) is the sum of the intact $(\text{DME-d}_6)_2^+$ dimer ms-TPES and its major ion fragment, deuterated DME monomer cation (see Figure 3). Vertical dashed lines in Figure 7 show the calculated VIEs for the three cation states of DME-d_6 monomer (see Table I) and the corresponding split states of the dimer isomers (see Table IV).

The ground $\tilde{X}^2B_1$ cation state of DME-d_6 can be thought of as the removal of an electron from the $2b_1$ HOMO of the neutral molecule, which has a *p*-orbital lone pair on the O atom and some C–D bonding character. The corresponding band maxima for the monomer and dimer are found at $10.11 \pm 0.04 \text{ eV}$ and $9.97 \pm 0.04 \text{ eV}$, respectively. Thus, dimerization of DME

causes a $\sim 140 \text{ meV}$ (between 60 and 220 meV) red shift in the valence band maximum, which is about 1/7 of the $\sim 1 \text{ eV}$ overall decrease in the position of the ground state band maximum observed previously³⁴ for DME clusters containing >2000 monomer units. More striking than the red shift in the band maximum is its broadening upon dimerization. The full width at half the band maximum increases from $0.3 \pm 0.1 \text{ eV}$ for the monomer to $0.6 \pm 0.1 \text{ eV}$ for the dimer, which corresponds to $\sim 2/3$ of the broadening observed when the monomer is compared with ultrafine DME-h_6 aerosol particles.³⁴ The broadening upon dimerization can at least in part be attributed to the existence of several stable, neutral isomers. Dashed lines in the lower panel of Figure 7 indicate the calculated VIEs for the 5 energetically close lying isomers of neutral DME dimer and illustrate similar broadening as observed in the experimental spectrum upon dimerization. As a result of the broadening and red shift in the maximum, the AE of the band decreases by 360 meV from $9.78 \pm 0.03 \text{ eV}$ for the monomer to $9.42 \pm 0.07 \text{ eV}$ for the dimer.

IV. CONCLUSIONS

We have presented threshold photoelectron photoion coincidence data of DME-h_6 and DME-d_6 monomer, dimer and their respective ion fragments in the photon energy range of 9–14 eV. Dimerization results in a red shift in the appearance energy of the ground state band in the TPES by $\sim 360 \text{ meV}$, a $\sim 140 \text{ meV}$ decrease of the band maximum, and a doubling of the peak width relative to the monomer.

Electronic structure calculations show that at least five isomers of DME dimer lie within $0.9 \text{ kcal mol}^{-1}$ of each other at a temperature of 100 K. The studied dimer isomers exhibit various C–H $\cdots$ O interactions. The C–H $\cdots$ O bond angles in the neutral dimer isomers range from 89° to 153° and are significantly narrower than the 172° C $\cdots$ H–O angle in the minimum energy, proton transferred dimer cation. Proton transfer in the ionized state was found to proceed without a barrier in all neutral dimer isomers and to result in the same optimized dimer cation geometry. The proton transfer reaction coordinate is complex and involves significant rearrangement of the monomer units. A large relaxation energy ($\sim 0.85 \text{ eV}$) due to the geometry change upon ionization of the DME dimer was found in the calculations. The experimentally observed AE does not correspond to the calculated AIE due to unfavorable Franck–Condon factors.

The ms-TPES was used to plot the breakdown diagrams which, together with the measured dissociation rates, were modelled to yield 0 K appearance energies. Both $(\text{DME-h}_6)_2$ and $(\text{DME-d}_6)_2$ dissociatively photoionize to form protonated and deuterated monomer with an onset of $AE_0 = 9.71 \pm 0.03 \text{ eV}$ and $9.73 \pm 0.03 \text{ eV}$, respectively. The onsets are equal within the experimental uncertainty, which is expected if there is no transition state at a higher energy than that of the final products. Thus, we have confirmed experimentally that the dissociation is governed by the product energies and not by a reverse barrier along the proton transfer or the dissociation reaction coordinate. Furthermore, because of good agreement between theory and experiment for the dissociative photoionization and ionization energies, the

calculated binding energy of the neutral dimer isomer 1 at 0 K of 2.9 kcal mol⁻¹ is a reasonable estimate.

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