

Barrierless proton transfer across weak CH...O hydrogen bonds in dimethyl ether dimer

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Proton transfer is of general interest due to the important role it plays in biological, chemical and atmospheric sciences. Hydrogen bonds are known to facilitate inter- and intra-molecular proton transfer, defining a coordinate for the transfer to proceed. The observation of protonated cluster fragments upon photoionization is typically explained by a fast intermolecular proton transfer occurring across hydrogen bonds. Hydrogen atom and proton transfer are common gas phase ion-molecule reactions of both polar and non-polar species. Therefore, clusters bound by weak van der Waals interactions, filling the gap between strongly hydrogen bonded systems and molecules interacting upon collision, are of particular interest for studying gas phase ionization-induced chemistry.

Dimethyl ether dimer is an example of a system that exhibits extremely weak, or arguably no hydrogen bonding. We present threshold photoelectron-photoion coincidence spectra of fully deuterated dimethyl ether monomer, dimer and their major ion fragments in the photon energy range of 9 to 14 eV. The lowest energy fragment ion arising from dissociation of the dimer is $\text{CD}_3\text{ODCD}_3^+$ with an appearance energy at 0 K of 9.730 ± 0.030 eV, which points to efficient ionization-induced intramolecular proton transfer. Results from electronic structure calculations confirm barrierless proton transfer in the ionized state of the dimer. The calculations suggest that at least five dimer isomers may have significant population in the molecular expansion. All neutral dimethyl ether dimer isomers studied exhibited only weak, unconventional hydrogen bonding, but were nevertheless found to undergo barrierless proton transfer upon photoionization producing the same isomer of the radical cation.

Primary author: Prof. SIGNORELL, Ruth (Laboratory of Physical Chemistry, ETH Zürich, Zürich, 8093, Switzerland)

Co-authors: Mr WEST, Adam H. C. (Laboratory of Physical Chemistry, ETH Zürich, Zürich, 8093, Switzerland); Dr BODI, Andras (Molecular Dynamics Group, Paul Scherrer Institut, Villigen, 5232, Switzerland); Dr YODER, Bruce L. (Laboratory of Physical Chemistry, ETH Zürich, Zürich, 8093, Switzerland); Prof. BRAVAYA, Ksenia B. (Department of Chemistry, Boston University, Boston, Massachusetts 02215-2521, USA)

Presenter: Prof. SIGNORELL, Ruth (Laboratory of Physical Chemistry, ETH Zürich, Zürich, 8093, Switzerland)

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