Hydrogen Bonding in Ion-pair Molecules in Vapors over ionic liquids, studied by Raman Spectroscopy and ab initio Calculations

Berg, Rolf W.

Publication date:
2010

Abstract for EUCHEM 2010 Conference on Molten Salts and Ionic Liquids
March 14-19, 2010 • Bamberg • Germany

[Session #: 1 or 2]

Hydrogen Bonding in Ion-pair Molecules in Vapors over ionic liquids, studied by Raman Spectroscopy and *ab initio* Calculations

Rolf W. Berg, *Department of Chemistry, Technical University of Denmark,*

Kemitorvet, Building 207, DK-2800 Lyngby, Denmark

The hydrogen bonding interactions in selected archetypal vapor molecules formed in the gas phase over protic ionic liquids are discussed, based on Raman spectroscopy assisted with *ab initio* molecular orbital DFT-type quantum mechanical calculations (B3LYP with 6-311+G(d,p) basis sets) on assumed gaseous free state models.
Some extreme examples are to be discussed: (1) The 1,1,3,3-tetramethylguanidinium chloride "molecule" [TMG-H-Cl] found[1] to exist in gaseous state over its corresponding liquid in evacuated ampouls heated at ~225°C (Fig. 1); (2) the analogous bromide "molecule" [TMG-H-Br][2] and (3) the 1-methylimidazolium ethanoate, [mim-H-O_2CCH_3] found[3] to have a less likely existence in the vapor of the corresponding liquid in ampouls at ~200°C (Fig. 2). Experimental Raman results will be compared to *ab initio* calculated spectra.

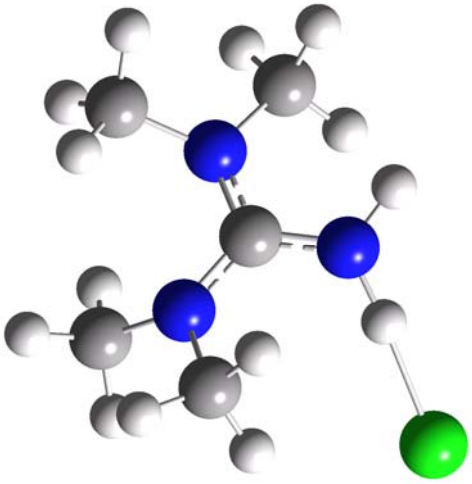

Fig. 1. Likely gaseous ion pair molecule of 1,1,3,3-tetramethylguanidinium chloride. The optimized N-H distance in the N-H···Cl bond was 1.099 Å. The H-Cl distance was 1.832 Å to compare with the ~1.27 Å in HCl gas. The bromide behaved similarly[2].

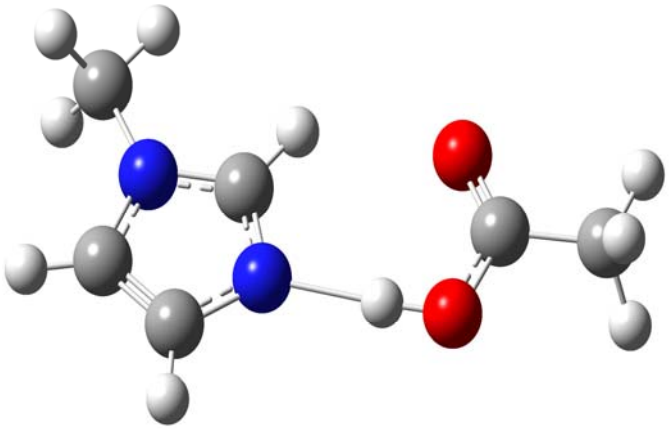

Fig. 2. Not so likely 1-methylimidazolium ethanoate gas molecule. The optimized N-H and H-O distances in the N-H···O bond were found as 1.730 and 1.005 Å. The comparable H-O distance in solid ethanoic acid is ~1.011 Å (neutron diffraction).

1 R. W. Berg, A. Riisager & R. Fehrmann, Formation of an ion pair molecule with a single NH^+···Cl^- hydrogen bond: Raman spectra of 1,1,3,3-Tetramethylguanidinium chloride, J. Phys. Chem. A, 2008, 112, 8585-8592.
2 R. W. Berg, O. Nguyen van Buu, A. Riisager. & R. Fehrmann, In preparation.
3 R. W. Berg, J.N.C. Lopes, L.P.N. Rebelo, K.R. Seddon & A.A. Tomaszowska, A Raman Spectroscopic Study of the Vapour Phase of 1-Methylimidazolium Ethanoate, a Protic Ionic Liquid, To be submitted for J. Phys. Chem. A (2009).