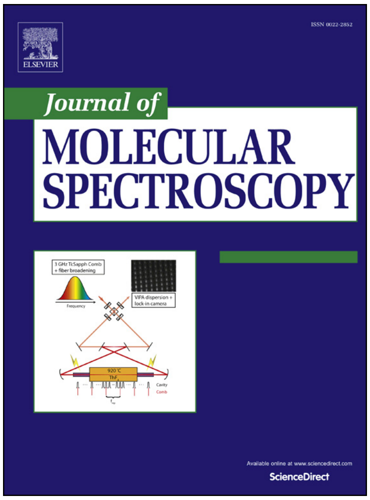
Microsolvation of the 5-hydroxyindole cation ($5HI^+$) with nonpolar and quadrupolar ligands: Infrared photodissociation spectra of $5HI^+$-L_n clusters with L=Ar and N_2 ($n \leq 3$)

Johanna Klyne, Otto Dopfer



PII: S0022-2852(17)30061-9
DOI: http://dx.doi.org/10.1016/j.jms.2017.03.010
Reference: YJMSP 10867

To appear in: *Journal of Molecular Spectroscopy*

Received Date: 31 January 2017
Revised Date: 7 March 2017
Accepted Date: 15 March 2017

Please cite this article as: J. Klyne, O. Dopfer, Microsolvation of the 5-hydroxyindole cation ($5HI^+$) with nonpolar and quadrupolar ligands: Infrared photodissociation spectra of $5HI^+$-L_n clusters with L=Ar and N_2 ($n \leq 3$), *Journal of Molecular Spectroscopy* (2017), doi: http://dx.doi.org/10.1016/j.jms.2017.03.010

Microsolvation of the 5-hydroxyindole cation ($5HI^+$) with nonpolar and quadrupolar ligands: Infrared photodissociation spectra of $5HI^+$-L_n clusters with L=Ar and N_2 ($n\leq3$)

Johanna Klyne and Otto Dopfer*

Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
*Corresponding author: Fax: (+49) 30-31423018, E-Mail: dopfer@physik.tu-berlin.de

revised version submitted to Journal of Molecular Spectroscopy on 7 March 2017
(invited contribution for special issue dedicated to Walther Caminati)

Abstract

Solvation of biomolecules and their building blocks has a strong influence on their structure and function. Herein we characterize the initial microsolvation of the 5-hydroxyindole cation ($5HI^+$) in its $^2A''$ ground electronic state with nonpolar and quadrupolar ligands (L=Ar, N_2) by infrared photodissociation (IRPD) spectroscopy of cold and mass-selected $5HI^+$-L_n ($n\leq3$) clusters in a molecular beam and dispersion-corrected density functional theory calculations (B3LYP-D3/aug-cc-pVTZ). The isomer-selective OH and NH stretch frequency shifts ($\Delta\nu_{OH/NH}$) disentangle the competition between H-bonding to the acidic OH and NH groups and π-stacking to the conjugated bicyclic aromatic π-electron system, the intermolecular interaction strengths, and the cluster growth sequence. For $5HI^+$-Ar_n, H-bonding and π-stacking strongly compete, indicating that dispersion forces are important for the interaction of $5HI^+$ with nonpolar ligands. In contrast, for $5HI^+$-$(N_2)_n$ clusters, the H-bonds are much stronger than the π-bonds and largely determine the initial solvation process. In all clusters, the OH…L bonds are stronger than the NH…L bonds followed by the π-bonds. The interaction of $5HI^+$ with N_2 is roughly twice stronger than with Ar, mainly due to the additional quadrupole moment of N_2. The nature and strength of the individual interactions are quantified by the noncovalent interaction approach. Comparison of $5HI^+$-L with the corresponding neutral clusters reveals the strong impact of ionization on the total and relative interaction strengths of the H-bonds and π-bonds. In addition, comparison of $5HI^+$-L with corresponding clusters of the phenol, indole, and pyrrole radical cations illustrates the effects of substitution of functional groups and the addition of aromatic rings to the various subunits of 5HI on the intermolecular potential.

Keywords

5-hydroxyindole, tryptamine alkaloids, solvation, hydrogen bond, stacking, molecular recognition