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Excitation of chiral molecules and their hydrated clusters by R2PI studies.

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1. Introduction.

Molecular clusters play a key role in the molecular scale explanations of macroscopic phenomena, being in between the isolated gas phase and the condensed phase. This condition allows to obtain information on intermolecular forces (dispersive, polarization, and electrostatic forces) simply by studying the physicochemical properties of isolated clusters and to extend them macroscopic systems. Weak interactions and hydrogen bond are particularly relevant both in inorganic as well as biological systems, characterized by high molecular and chiral selectivity.

Molecular-scale understanding of intermolecular forces and solvation effects can be performed through gas phase methodologies as laser spectroscopy and mass spectrometry [1,2]. Only recently these methodologies have been applied to study the physicochemical properties of chiral systems [3-5], while in condensed phase enantioselective intermolecular interactions have been studied in the past by various techniques (NMR, CD, Chromatography).

In this paper we report on a comprehensive study of the short-range forces operating in the molecular complexes between several chiral aromatic alcohols (M) and water (*solv*), through the application of mass resolved REMPI technique.

2. Experimental methodology.

The experimental setup, which combines a supersonic molecular beam, two Nd-YAG pumped dye lasers and a time of flight (TOF) mass spectrometer, has been already described [5]. Supersonic beam production of the adducts is obtained by adiabatic expansion of a carrier gas (Ar) seeded with a selected chromophore M and partners *solv* through a heatable pulsed nozzle of 400 μm i.d. The concentration is maintained enough low to minimize the contribution of heavier clusters to the spectra. The skimmed supersonic jet (1 mm skimmer diameter) enters into a second chamber equipped with a TOF mass spectrometer. Molecules and clusters in the beam are excited and ionized by one or two tunable dye lasers pumped by the same Nd-YAG laser and the ionized species are detected by a channeltron. The mass selected photoionization signals are recorded and averaged by a digital oscilloscope and stored on a PC.

One colour R2PI experiments (1cR2PI) involve electronic excitation of the species of interest by absorption of one photon $h\nu_1$ and by its ionization by a second photon $h\nu_2$. Mass discrimination of the ionized complex may be complicated by its fragmentation, due to the excess energy gained in ionization process [4, 6-7].

The photoionization efficiency curves have been obtained by two colour R2PI (2cR2PI) sequence: i- the first exciting laser ($h\nu_1$) is tuned on the $S_1 \leftarrow S_0$ transition of the species of interest; ii- the laser intensity is lowered to about 1% of the initial fluence to minimize the $h\nu_1$ absorption; iii- a second laser ($h\nu_2$) is scanned through the cluster ionization and fragmentation threshold regions. The photoionization spectra were corrected for the effect of

the electric field strength (200 V/cm) produced by the extraction plates of the TOF spectrometer.

The binding energy D_0^* of the *M-solv* adduct is computed from the difference between its dissociative ionization threshold $AE(M)^+ = h\nu_1(M-solv)^+ + h\nu_2(M^+ + solv)$ and the ionization threshold of bare *M*, i.e. $IP(M) = h\nu_1(M)^+ + h\nu_2(M)^+$. The dissociation energy D_0^* of the ionic cluster $(M-solv)^+$ is calculated from the difference between its dissociative ionization threshold, $AE(M)^+ = h\nu_1(M-solv)^+ + h\nu_2(M^+ + solv)$, and its ionization threshold $IP(M-solv) = h\nu_1(M-solv)^+ + h\nu_2(M-solv)^+$.

3. The hydration of aromatic molecules.

Hydrated aromatic molecules are simple model systems for the study of selectivity and function of biologically active systems. The role of hydrogen bond interaction and molecular conformation in these systems has been studied for many aromatic molecule-water systems [6] and also on molecules of biological interest [8]. R2PI studies of hydrated clusters of lead alcohols are reported. The measure of shifts and binding energy of these systems can lead information on the behaviour of water, which can act both as proton donor and proton acceptor.

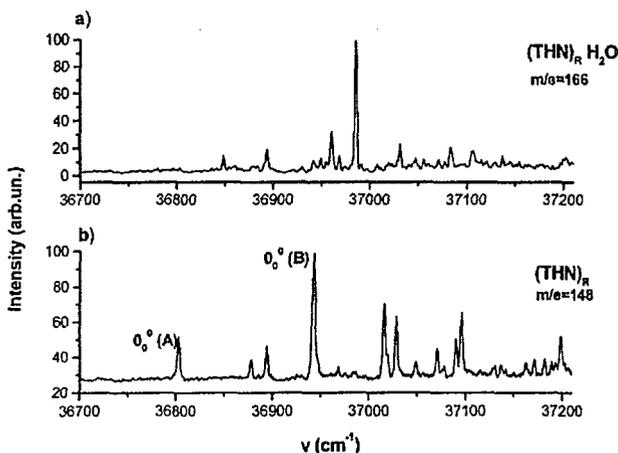


Figure 1 Mass-resolved one colour R2PI excitation spectra of THN_R (a) and THN_R-H_2O (b), measured respectively at $m/z = 148$ and $m/z = 166$, and at a total stagnation pressure of 3 bar.

In fig. 1, the one colour R2PI spectra of 1-tetralol (THN_R) and THN_R-H_2O are shown. The two bands marked in the spectrum are tentatively assigned to the two axial and equatorial conformers of THN_R . As already found for 1-phenyl-1-ethanol-water and 1-phenyl-1-propanol-water clusters a blue shift with respect to the 0_0^0 electronic transition $S_1 \leftarrow S_0$ of the chromophore is observed. A blue shift reflects the fact that the interaction forces decrease upon excitation. The blue shift of the electronic transition in many 1:1 aromatic molecule-water cluster is not unusual and can be related to a $O-H \cdots \pi$ interaction between water and the chromophore, in which water acts as proton donor [8,9].

In fig. 2b the one colour R2PI spectra of 1-indanol (I_R) is reported. The two stable conformers predicted from *ab initio* calculation for I_R molecule, cannot be easily assigned in the spectrum. The spectra of the two conformers could be superimposed within $1-2 \text{ cm}^{-1}$. A

few vibronic bands calculated in the harmonic calculations, are marked in the spectrum. Experimental shift of the 0^0_0 electronic transition for $I_R\text{-H}_2\text{O}$ (fig. 2a) is around 0 cm^{-1} . At variance with other non cyclic benzylic alcohols, calculations for $I_R\text{-H}_2\text{O}$ predict that in the most stable structure, I_R acts as a proton acceptor towards water, and the O—H \cdots π interaction is negligible.

The combination of mass selected R2PI technique and *ab initio* computation has proven to be an efficient tool in the study of the hydrated clusters of benzylic alcohols produced in the low temperature environment of a supersonic beam.

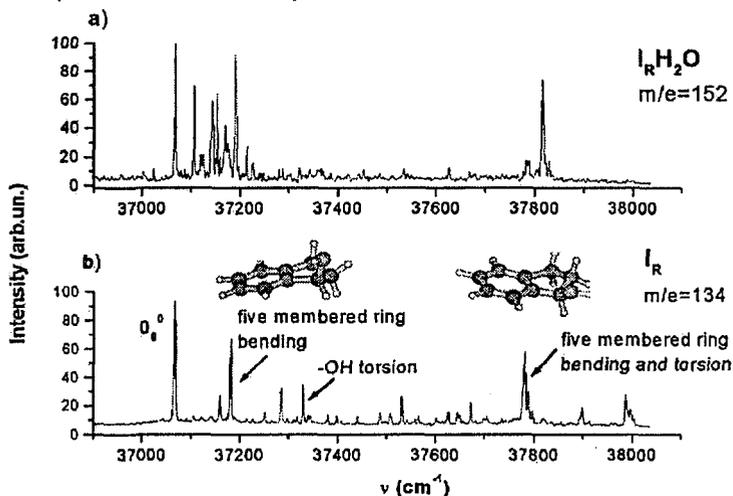


Figure 2 Mass-resolved one colour R2PI excitation spectra of I_R (a) and $I_R\text{-H}_2\text{O}$ (b), measured respectively at $m/z = 134$ and $m/z = 162$, at a total stagnation pressure of 3 bar.

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