

Resonance enhanced multiphoton ionization processes to study spectroscopy and reactivity of van der Waals clusters of aromatic molecules

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Abstract. One colour resonance enhanced two photon ionization of van der Waals complexes of (R +)-1-phenyl-1-propanol clustered with chiral and non chiral compounds have been studied. Enantiodifferentiation, different fragmentation patterns and reactivity are discussed on the basis of experiments.

Keywords. REMPI; enantiodifferentiation; fragmentation; proton transfer.

1. Introduction

A large number of weakly bound clusters of solvated aromatic molecules have been studied in recent years^{1–4}. The isolated aggregates of one or several solvent molecules with the solute aromatic compound can be produced by the jet cooled supersonic beam technique, which consists of a carrier gas seeded with the aromatic chromophore and other partners expanded through a pulsed nozzle. Supersonic beam parameters such as temperature and stagnation pressure can influence the size distribution of the clusters¹. The advantage of this technique is threefold. First, only the lowest rotational and vibrational levels in the electronic ground state are populated leading to less congested spectra. In addition, the photochemical and photophysical properties can be studied without the interference of the medium as it happens in conventional condensed phase. Finally, the low internal temperature permits stabilization of structural variants and of molecular clusters. Although for most of the van der Waals systems studied, accurate potential energy surface (PES) are not available, a semiempirical computational method amenable to draw some conclusion on the cluster geometries has been developed^{5,6}. In most of the substituted aromatic molecules, various binding sites leading to stable structures were predicted⁷. The coexistence of several isomers into the supersonic molecular beam has been indeed experimentally demonstrated for aniline and styrenes confirming the structure calculations^{7,8,9}.

A significant amount of information on the properties of isolated clusters can be obtained by combining this molecular beam technique with one colour and two colour resonant enhanced multi photon ionization (REMPI) spectroscopy and mass analysis^{6,7}. The resonant two photon excitation spectrum (R2PI) of the mass resolved cluster is characterized by a shift of the 0_0^0 electronic origin with respect to the bare

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aromatic chromophore. This spectral shift represents the difference in binding energies in the electronic excited and ground states of each cluster investigated and is peculiar of its structural properties. Moreover the mass analysis of the compounds can give evidence of fragmentation processes and intracuster reactions.

In this paper, we have applied this mass resolved spectroscopy to study a chiral molecule, the R 1-phenyl 1 propanol (P_R), pure and clustered with different solvent molecules. The specificity of the spectral shift induced by the binding of a chiral molecule has been demonstrated studying clusters of this molecule with R and S butanol (B_R , B_S) and with R and S 2-butylamine (N_R , N_S). Clusters with other molecules such as water, methanol and ethanol which give rise to vdW and hydrogen bonding and with argon, methane and butane have also been studied. In this investigation not only the spectral shifts, but also the reaction patterns of the clusters upon ionization have been reported. When hydrogen bonding is the most important interaction, the ethyl loss fragmentation process is the dominant dissociation channel.

2. Experimental

The apparatus for cluster beam generation and REMPI has been previously described^{5,6} and therefore only its main features are reported here. The supersonic pulsed beam is produced by adiabatic expansion, through a 400 μm nozzle, of Ar carrier gas seeded with the R aromatic chromophore and the solvent molecules. The pulsed nozzle and the inlet system can be heated up to 150°C. The molecular beam passes through a 1 mm skimmer into a second chamber equipped with a time-of-flight (TOF) mass spectrometer. Molecules and clusters are ionized by REMPI and the ions are detected by a channeltron after a 50 cm flight length. The laser system consists of a frequency doublet Nd: YAG ($\lambda = 532$ nm) which pumps two dye lasers. The dye outputs are doubled and when necessary mixed with residual 1064 nm radiation to obtain two independent frequencies ν_1 and ν_2 . Neutral compounds in the supersonic beam are excited to the S_1 state through ν_1 and then ionized by a one or two colour REMPI process. The ions thus produced are detected by a TOF mass spectrometer. The amplified ionic signal is recorded by a digital oscilloscope and is computer processed. Excitation spectra of the bare molecule and the formed clusters can be measured by recording the ion signal at each mass peak as a function of ν_1 . In a one-colour ionization process some excess energy can be imparted to the system and fragmentation or other reaction processes like dissociative proton transfer (DPT), dissociative electron transfer (DET) and nucleophilic substitution, can take place³. The excitation spectra may thus be observed also at the mass of the products. Photons of different colour have been used to measure the appearance potential of the molecule or clusters in a two-colour resonant two photon ionization (R2PI) process. In this experiment the compounds are excited to the S_1 state by the first photon at fixed ν_1 frequency and the frequency of the second ionizing photon ν_2 is varied.

3. Results and discussion

Electronic ground state structure and vibrational frequencies of 1-phenyl-1-propanol molecule were calculated by the density functional method¹⁰. Semiempirical methods based on Lennard Jones, hydrogen bonding, and coulomb atom-atom interactions have been used to describe the intermolecular potential in the cluster¹¹. In figure 1 the

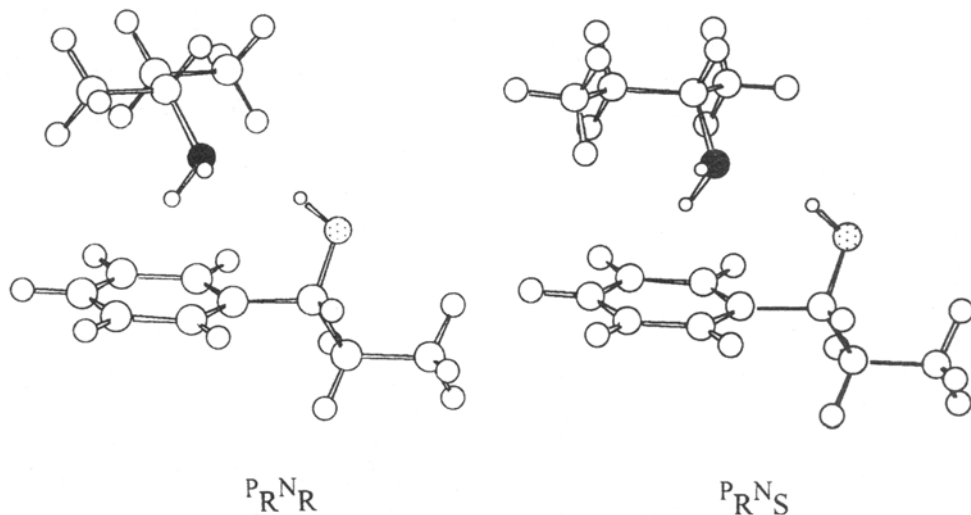


Figure 1. Predicted structures for the $P_R N_R$ and $P_R N_S$ clusters.

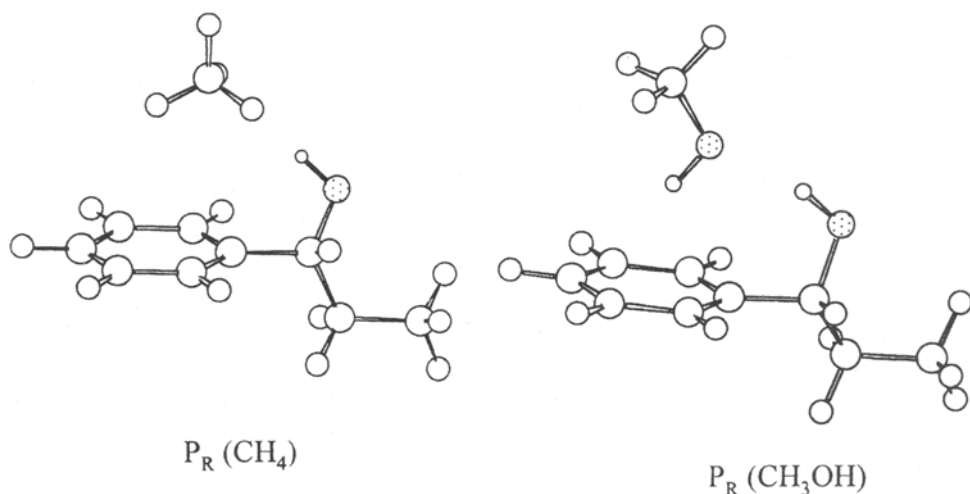


Figure 2. Predicted structures for the $P_R(CH_4)$ and $P_R(CH_3OH)$ clusters.

predicted structures of $P_R N_R$ and $P_R N_S$ clusters are shown. In figure 2 analogous structures for P_R clustered with methane and methanol are reported. In figure 3 the excitation spectra of the R 1-phenyl 1-propanol molecule is reported up to 1000 cm^{-1} with respect to the electronic $S_0 \leftarrow S_1$ origin found at 37577 cm^{-1} . Few vibronic transitions have been identified. The low frequency modes can be assigned to the torsional motion of the ring substituent (41 and 47 cm^{-1}). The other intense features can be attributed to typical skeletal and group frequencies of the aromatic molecule¹⁰. In figure 4 typical time-of-flight mass spectra of the R chromophore mixed with CH_4 and CH_3OH taken at the resonance frequencies of the clusters is shown. Both clusters fragment upon ionization because of the excess energy furnished. A different behaviour is found for the two

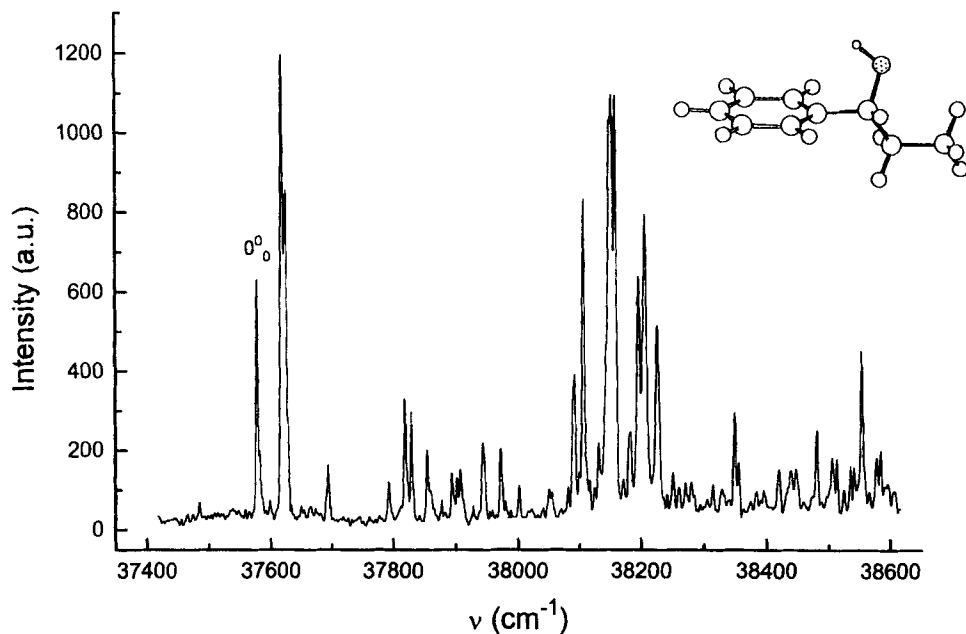


Figure 3. One colour R2PI spectrum of (R+)1-phenyl-1-propanol taken at $m/e = 136$ at a total stagnation pressure of $2 \cdot 10^5$ Pa. Predicted structure for the S_0 state is also reported.

clusters. The $P_R(\text{CH}_4)$ cluster dissociates mainly through separation of the solute solvent moieties, while the $P_R(\text{CH}_3\text{OH})$ cluster dissociates into two fragments, P_R and $[P_R(\text{CH}_3\text{OH})]-\text{C}_2\text{H}_5$, having an almost equal intensity. To gain some insight into the origin of this ethyl loss, the unknown ionization potential of the P_R molecule has been determined through a 2CR2PI experiment. A value of 8.84 ± 0.01 eV has been found. The excess energy furnished in a one colour two photon ionization process (~ 0.3 eV) is enough to dissociate the cluster, while a simple $1 + 1$ resonant two photon ionization hardly accounts for the type of ion fragmentation observed. It can therefore be concluded that the fragment ions presumably arise from resonant $1 + 2$ three photo ionization events.

For other solvents forming hydrogen bonding, namely water, alcohols and amines, the main fragmentation pattern invariably corresponds to ethyl loss. This indicates the presence of an effect due to hydrogen bonding, which could perturb the cluster energetics with the consequent weakening of the C–C bond.

The excitation spectra of other adducts studied, (not reported here for sake of brevity,) have been recorded at the mass peak of the cluster or when complete dissociation takes place at the mass of the fragment. In case of $P_R(\text{Ar})$ and $P_R(\text{CH}_4)$ the excitation spectra have been determined by taking into account the spectra of the P_R molecule in pure He. All these clusters display a complex, not easily attributable, vibronic spectrum due to the numerous vdW vibrations possibly coupled with low frequency modes of the molecules¹². The spectra are differently shifted with respect to the 0_0^0 electronic origin of the molecule. In particular, when P_R is linked to a water molecule a blue shift of 87 cm^{-1} has been found, indicating a weakening of the binding energy in the excited state. For CH_4 and $n\text{C}_4\text{H}_{10}$ solutes, the absorption spectrum is

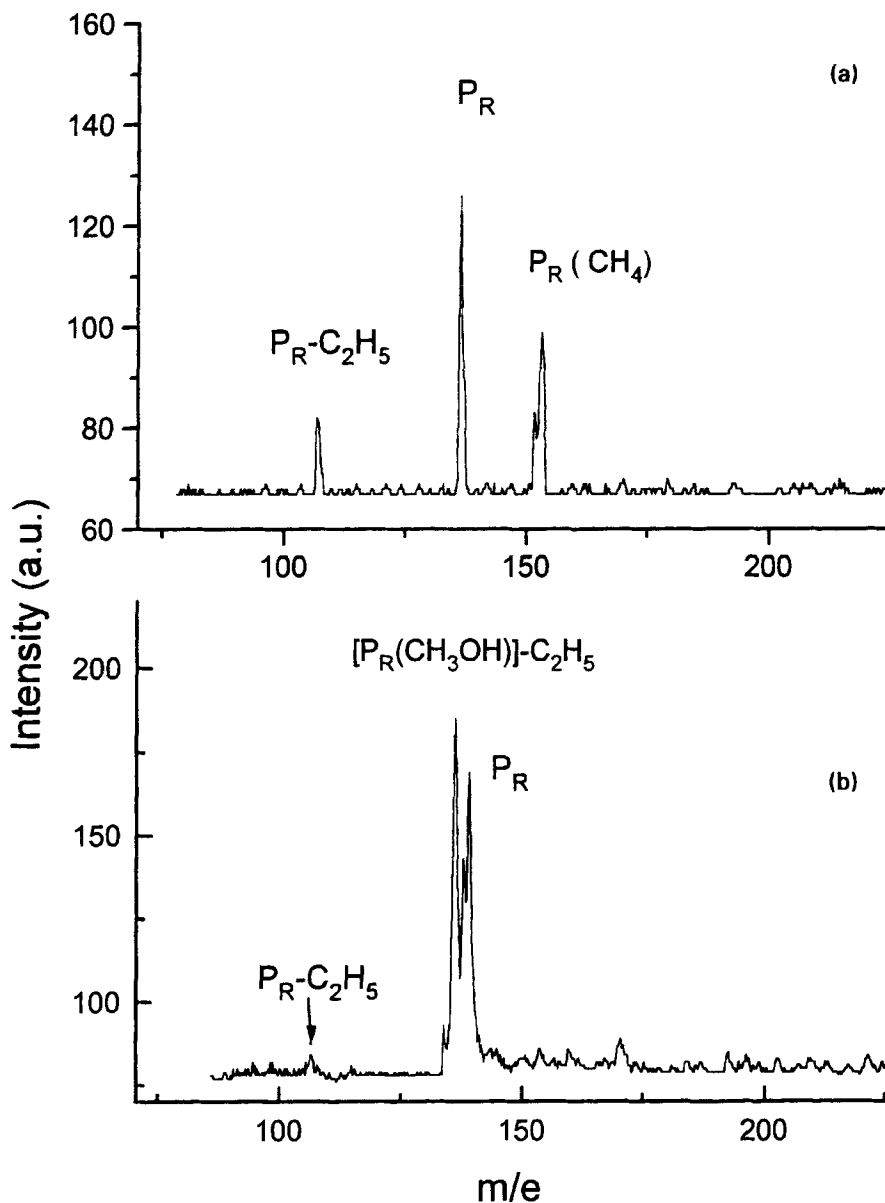


Figure 4. Time-of-flight mass spectrum of (R+)1-phenyl-1-propanol clustered with (a) CH_4 at $\lambda = 264.37$ nm and (b) CH_3OH at $\lambda = 265.97$ nm at a total stagnation pressure of $2 \cdot 10^5$ Pa.

red shifted of -36 and -20 cm^{-1} respectively with regard to the bare molecule, indicating that in the excited S_1 state the binding energy is larger than in the ground S_0 state. In the alcohol series, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_4\text{H}_9\text{OH}$, the red shift increases with the increase of the alkylic group size in agreement with the prediction that the dispersive interactions are more and more stronger¹. In table 1, the measured shifts for the clusters studied are reported.

Table 1. Measured shifts for different clusters of (R +)-1-phenyl-1-propanol relative to the 0% electronic origin of the $S_0 \leftarrow S_1$ transition of the bare molecule

Ar	CH ₄	nC ₄ H ₁₀	H ₂ O	(H ₂ O) ₂	CH ₃ OH	C ₂ H ₅ OH	2-ButOH (R -)	2-ButOH (S +)	2-ButNH ₂ (R -)	2-ButNH ₂ (S +)
shifts (cm ⁻¹)	-27	-36	-20	87	20	-3	-80	-92	-109	-127

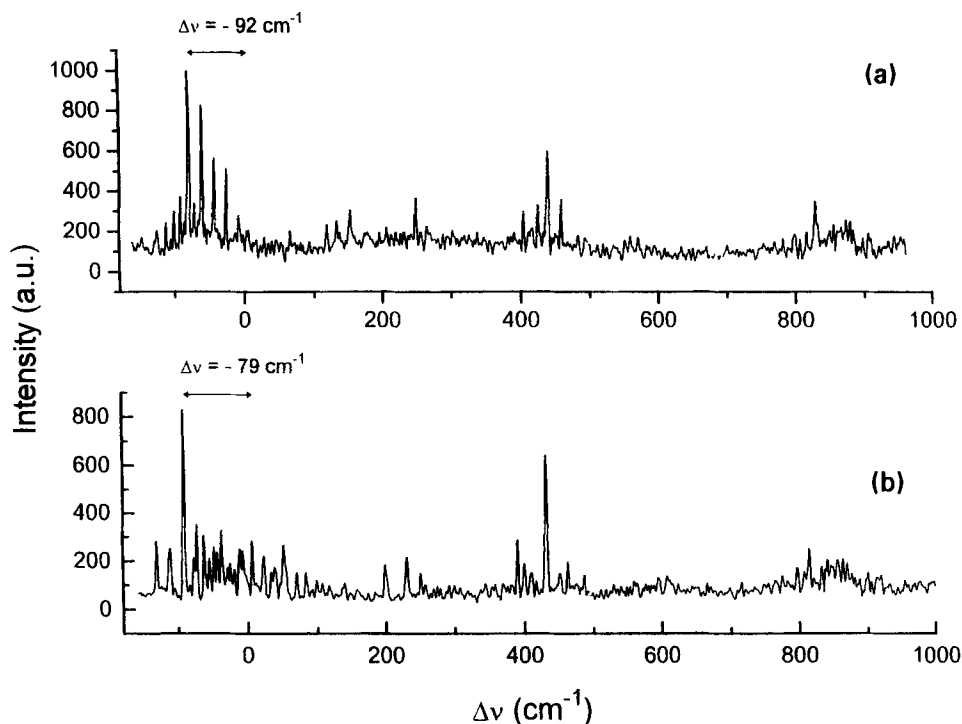


Figure 5. One colour R2PI spectrum of (R +) 1-phenyl-1-propanol clustered with (a) (R -) 2-butanol and (b) (S +) 2-butanol, taken at $m/e = 181$. The zero on the frequency scale is relative to the 0_0^0 electronic origin of the $S_0 \leftarrow S_1$ transition of 1-phenyl 1-propanol at 37577 cm^{-1} .

When distinct optically active compounds, in turn R or S 2-butanol or R or S 2-butylamine, are introduced as solvating agents, different spectral behaviour is observed for the two diastomeric pairs, from which the enantiomers could be distinguished. Chiral recognition is evidenced by the different spectral signatures of the two diastomeric complexes, namely the electronic band origin and their vibronic bands. The time-of-flight mass spectra of the P_R chromophore mixed with the R or S 2-butanol molecule (B_R and B_S), taken at the resonance frequency of $P_R B_R$ and $P_R B_S$ clusters were previously reported¹³. The mass analysis of the undissociated cluster ($m/e = 210$) together with other ions originating from solute solvent dissociation and fragmentation with ethyl loss ($m/e = 181$ and 107) showed that for the heterochiral cluster $P_R B_S$ the intensity ratio of the fragments with respect to that of the cluster at $m/e = 210$, is higher. This fact denotes that at equal excitation levels, the $P_R B_R$ ions are less prone to fragmentation than those from $P_R B_S$. The spectra of P_R clustered with the two B_R and B_S enantiomers around the 0_0^0 electronic band origin of the $S_0 \leftarrow S_1$ transition of the molecule are reported in figures 5a and b. A different bathochromic shift of the electronic band origin is observed. The shifts of the most intense bands which can be tentatively assigned to the electronic origin of the clusters differ by a $\Delta\nu = 12 \text{ cm}^{-1}$, being the band of the $P_R B_R$ complex shifted by a $\Delta\nu = -92 \text{ cm}^{-1}$ and the $P_R B_S$ by a $\Delta\nu = -79 \text{ cm}^{-1}$. The larger shift for the $P_R B_S$ complex indicates that in

the excited cluster, strengthening of the attractive interactions tends to reduce or even to invert the weak bonding difference which characterizes the ground state¹⁴. In the spectrum of the chromophore mixed with B in racemic form both the band systems attributed to $P_R B_R$ and $P_R B_S$ complexes are found. It should be noted that, when a more efficient cooling is achieved, the relative band intensities change and the formation of $P_R B_R$ complex is slightly enhanced. This can be due to a more favoured

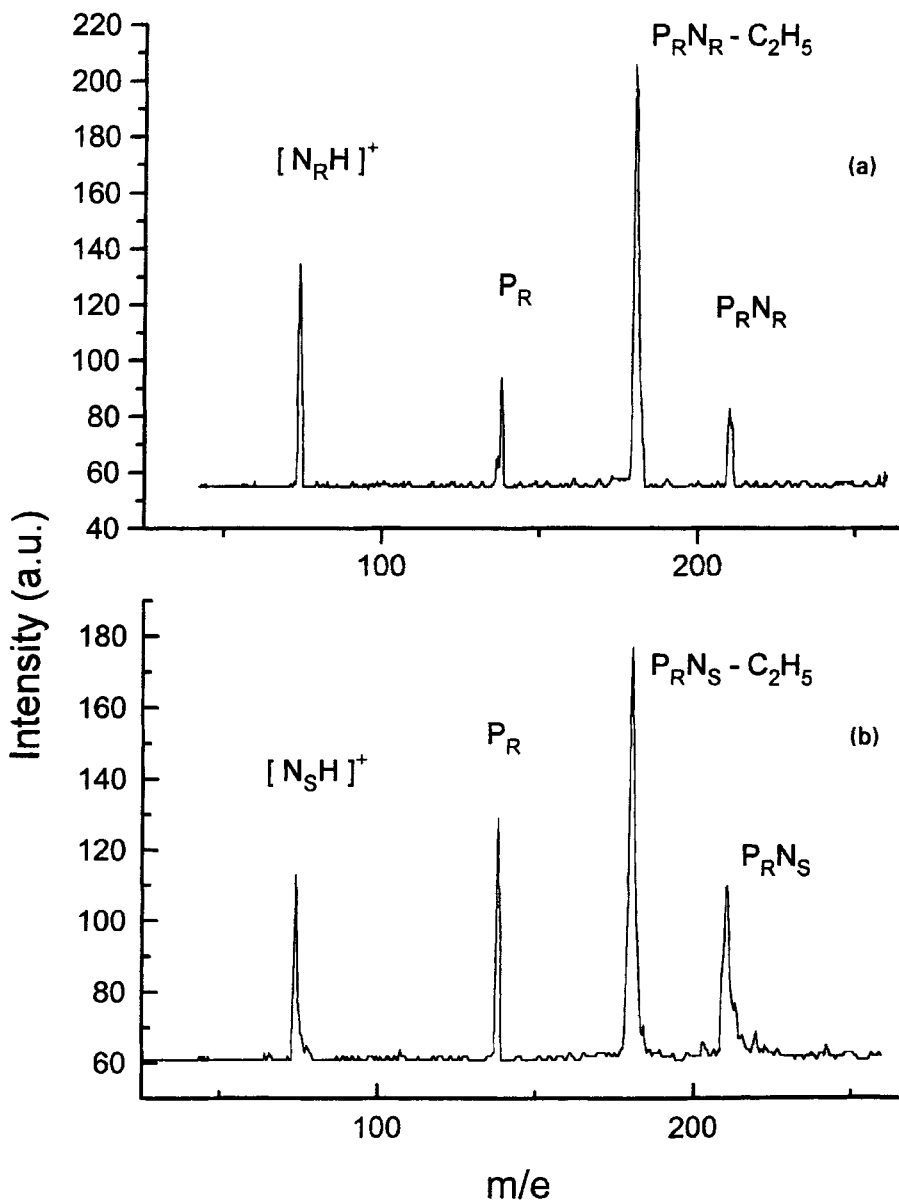


Figure 6. Time-of-flight mass spectrum of (R +) 1-phenyl-1-propanol with (a) (R -) 2-butylamine at $\lambda = 266.89$ nm and (b) (S +) 2-butylamine at $\lambda = 267.00$ nm at a total stagnation pressure of $2 \cdot 10^5$ Pa.

structure of this adduct, in agreement with molecular mechanics calculations¹⁴. When P_R is clustered to 2 butylamine, dissociated and fragmented ions are detected in the mass spectrum together with an ion at $m/e = 74$ corresponding to dissociative proton transfer (DPT) (figures 6a, b). Intracluster reactivity between ionized aromatic molecules and amines has been previously observed and appropriately related to solute and solvent ionization potentials and proton affinity of the different amines investigated [6, 3]. A clear enantiodifferentiation was found for the different diastereomer pairs $P_R N_R$ and $P_R N_S$ as shown by the excitation spectra reported in figures 7a, b. The shifts differ by 18 cm^{-1} being the shift of the $P_R N_R$ cluster -109 cm^{-1} with respect to the bare molecule and that of the $P_R N_S$ cluster -127 cm^{-1} . This fact confirms that it is possible to discriminate vdW diastereomeric complexes formed by supersonic expansion.

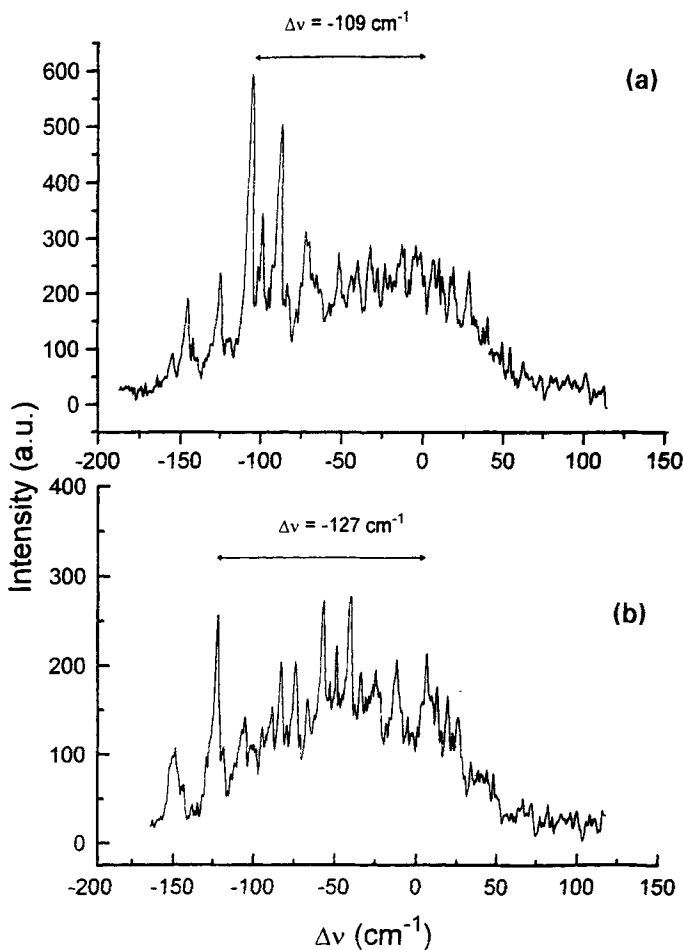


Figure 7. One colour R2PI spectrum of (R +) 1-phenyl-1-propanol clustered with (a) (R -) 2-butylamine and (b) (S +) 2-butylamine, taken at $m/e = 180$. The zero on the frequency scale is relative to the 0_0^0 electronic origin of the $S_0 \leftarrow S_1$ transition of 1-phenyl 1-propanol at 37577 cm^{-1} .

Conclusions

The present studies have explored the potentiality of the REMPI technique applied to mass spectrometry and spectroscopy of cluster of a chiral chromophore with different solvents. It has been proven that the technique is highly selective to enantiodifferentiate neutral chiral molecules. The complexation of a chiral molecule with a suitable chiral solvent causes indeed a different spectral signature. Comparison among the mass spectra reveals differences in the fragmentation patterns which are enough to allow discrimination between the diastereomers. The large fragmentation of the cluster at resonance wavelength could be applied to obtain enrichment in a racemic mixture. Differences in absorption frequencies in gas phase (CF_3Br) and in supersonic jets have been previously utilized in the isotopic enrichment process¹⁵ and the same technology could be applied to racemic mixtures to enantiomerically enrich a racemate.

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