Photochemical R2PI study of chirality and intermolecular forces in supersonic beam

A. Giardini Guidoni,[1,3,†] S. Piccirillo,[2] D. Scuderi,[1,4] M. Satta,[1]
T. M. Di Palma,[3] M. Speranza,[4] A. Filippi,[4] and A. Paladini[1]

[1] *Dipartimento di Chimica, Universita' di Roma "La Sapienza", Pl. A. Moro 5, I-00185 Roma, Italy*

[2] *Dipartimento di Scienze e Tecnologie Chimiche Universita' di Roma "Tor Vergata"*
Via della Ricerca Scientifica, 00133 Roma, Italy

[3] *CNR-Istituto Materiali Speciali, I85050 Tito Scalo (Pz), Italy*

[4] *Dipartimento di Studi di Chimica e Tecnologie delle Sostanze Biologicamente Attive*
Universita' di Roma "La Sapienza" Pl. A. Moro 5, I-00185 Roma, Italy

ABSTRACT. One and two-color, mass selected R2PI spectra of the $S_1 \leftarrow S_0$ transitions in the bare *(+)-(R)-1-phenyl-1-ethanol* (**E_R**) and its complexes with different solvent molecules (**solv**) *(−)-(R)-2-butanol* (**B_R**) or *(+)-(S)-2-butanol* (**B_S**), *(−)-(R)-2-pentanol* (**T_R**) or *(+)-(S)-2-pentanol* (**T_S**) and *(−)-(R)-2-butylamine* (**A_R**) or *(+)-(S)-2-butylamine* (**A_S**), have been recorded after a supersonic molecular beam expansion. The one-color R2PI excitation spectra of the diastereomeric complexes are characterized by significant shifts of their band origin relative to that of bare **E_R**. The extent and the direction of these spectral shifts are found to depend upon the structure and the configuration of **solv** and are attributed to different short-range interactions in the ground and excited states of the complexes. In analogy with other diastereomeric complexes, the phenomenological binding energy of the homochiral cluster is found to be greater than that of the heterochiral one. Preliminary measurements of excitation spectrum of *(+)-(R)-1-Indanol* (**I_R**) is also reported.

1. INTRODUCTION

The study of chirality and enantiomerism has attracted the interest of many scientists due to implication of these properties in many different fields [1]. Enantiomers possess identical properties as long as they are exposed to an achiral environment. However once presented to a handed surrounding, image and mirror image will be differently recognized. Many chemical and biological reactions display a pronounced enantioselectivity, which can be abscribed to the different interactions between chiral molecules in diastereomeric complexes. The interpretation of chiral discrimination in terms of the weak association forces in molecular aggregates is difficult in the condensed phase due to the unavoidable presence of the solvent molecules. Studies of physicochemical properties of chiral systems in solvent free conditions have been performed by resonant laser spectroscopy and mass spectrometry under suitable conditions. In particular the gas phase recognition of chirality is based on the different properties of diastereomeric complexes between a chiral molecule (**C**) and a chiral solvent (**solv**). Weakly bound aggregates are formed in supersonic molecular beam expansion at sufficiently low temperatures ($< 10^\circ$ K) that entropy-enthalpy compensation effects are negligible. Chiral discrimination is based on the binding energy differences in the diastereomeric clusters. Mass-resolved resonant two-photon-ionization (R2PI) coupled with time of flight (TOF) mass spectrometry is the technique used to measure these differences in stability [1, 2].

Ionization and fragmentation potentials of bare chromophores **C** and their clusters with **solv** provide a measure of the binding energy of the diastereomeric clusters in their ground and ionized states. In order to clarify the structure of unsolvated diastereomeric aggregates and to define the nature of the intra-complex interactions, spectral assignment and measured binding energy values can be compared with ab initio theoretical predictions.

In a previous paper, we have reported R2PI studies of spectroscopic properties and of the relative stability of clusters between a chiral aromatic chromophore *(+)-(R)-1-phenyl-propanol* (**P_R**) and various solvent molecules, such as chiral alcohols and chiral amines. These studies gave insights into the attractive and repulsive forces operating in these systems, and it was found that the homochiral complexes are more stable than the heterochiral ones [1–5].

We have extended these studies to other chromophores **C** as *(+)-(R)-1-phenyl-1-ethanol* (**E_R**) which has a shorter side chain with respect to *(+)-(R)-1-phenyl-1-propanol* (**P_R**) and *(+)-(R)-1-Indanol* (**I_R**) in which a ring closing of alchilic side chain is present, with the aim to

[†] E-mail: anna.giardini@uniroma1.it

study the effect of the lateral chain of the chromophore on the chemical properties of the diastereomeric clusters. In this paper studies of the diastereomeric complexes between *(−)-(R)-2-butanol* ($\mathbf{B_R}$), *(+)-(S)-2-butanol* ($\mathbf{B_S}$), *(−)-(R)-2-pentanol* ($\mathbf{T_R}$), *(+)-(S)-2-pentanol* ($\mathbf{T_S}$), *(−)-(R)-2-butylamine* ($\mathbf{A_R}$) and *(+)-(S)-2-butylamine* ($\mathbf{A_S}$) and the *(+)-(R)-1-phenyl-1-ethanol* ($\mathbf{E_R}$), and preliminary results on the bare *(+)-(R)-1-Indanol* ($\mathbf{I_R}$) are reported.

2. EXPERIMENTAL

2.1. Procedure. 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 [6]. Molecules and clusters in the beam are resonantly ionized by two photons coming from tunable dye lasers pumped by the same Nd-YAG laser. The ionized species are analyzed by TOF-MS. One color R2PI experiments (1cR2PI) involve electronic excitation of the species of interest by absorption of one photon $h\nu_1$ and ionization by a second photon of the same color.

Photoionization efficiency curves have been determined by the 2cR2PI sequence: i) the first exciting laser ν_1 is tuned on the $S_1 \leftarrow S_0$ transition of the species; ii) the laser intensity is lowered to minimize the $h\nu_1$ laser absorption; iii) a second laser ($h\nu_2$) is scanned through the cluster ionization and fragmentation threshold regions. The binding energy $D"_0$ of the $\mathbf{E_R solv}$ adduct in the ground state is then computed from the difference between its dissociative ionization threshold $AE(\mathbf{E_R}^+) = h\nu_1(\mathbf{E_R solv})^* + h\nu_2(\mathbf{E_R}^+ + \mathbf{solv})$ and the ionization threshold of bare chromophore $IP(\mathbf{E_R})(= h\nu_1(\mathbf{E_R}^*) + h\nu_2(\mathbf{E_R}^+)$.

2.2. Computational details. The electronic ground state structure and vibrational frequencies of $\mathbf{E_R}$ were computed by density functional calculations based on Becke's three parameter hybrid functional includying the LYP correlation functional (B3LYP); the 631G** gaussian split valence basis set, in which *p* functions are added to H atom and *d* functions to heavy atoms, was used. The ab initio calculations were performed using the Gaussian 98 package [7]. The E_R *IP* has been calculated as the difference between the total energies of the optimized neutral and ionic E_R molecules. These calculations have been performed by the Modified Neglecting Differential Overlap (MNDO) semiempirical method [8], with a set convergence fixed at 0.04 KJ/mol. The geometry optimization was computed using the Polak-Ribierre (conjugated gradient) algorithm in which the convergence threshold was 0.04 KJ/mol.

3. RESULTS AND DISCUSSION

3.1. Excitation and ionization spectra of the bare chromophores $\mathbf{I_R}$ and $\mathbf{E_R}$ and its molecular cluster with $\mathbf{B_{R/S}}$, $\mathbf{T_{R/S}}$ and $\mathbf{A_{R/S}}$. The excitation spectrum of the bare chromophore $\mathbf{E_R}$, taken up to 1000 cm^{-1} above the $S_1 \leftarrow S_0$ electronic origin at 37618 cm^{-1}, has been already reported [5, 9]. Briefly only one stable conformer was identified together with some vibronic transitions of $\mathbf{E_R}$ in the S_1 excited state. B3LYP/6-31G** calculations point to just one stable conformer for the $\mathbf{E_R}$ molecule in agreement with the experimental observations. Measurement of the experimental *IP* of this molecule is 8.89 eV in fair agreement with the adiabatic calculated value [10].

Diastereomeric clusters formed in the supersonic expansion between the $\mathbf{E_R}$ chromophore and $\mathbf{B_R}$, $\mathbf{B_S}$ and $\mathbf{T_R}$, $\mathbf{T_S}$ chiral alcohols and $\mathbf{A_R}$, $\mathbf{A_S}$ chiral amines, have been investigated using 1cR2PI technique. Several conformers may be generated by supersonic expansion of mixtures of $\mathbf{E_R}$ with these **solv**, and their vibronic transitions generally complicate the mass resolved excitation spectra. Other peaks in the spectra may arise from extensive fragmentation of larger clusters. The excitation spectra of the heterochiral complexes $\mathbf{E_R B_S}$ and the homochiral one $\mathbf{E_R B_R}$ at m/e = 196 have been already reported [5]. Both diastereomeric clusters display a structured vibronic spectrum due to the presence of various conformers and/or to vibronic transitions. The most intense band of the spectrum, assigned to the electronic band origin of the cluster, is red-shifted relative to that of the bare chromophore, at 37618 cm^{-1}. This indicates that the chromophore acts as a proton donor [3] and that the binding energy of the adducts is greater in the S_1 state than in the S_0 state [3, 11, 12]. The red shift of the heterochiral complex ($\Delta\nu = -131\ cm^{-1}$) exceeds that of the homochiral one ($\Delta\nu = -119\ cm^{-1}$) by $\Delta(\Delta\nu) = 12\ cm^{-1}$.

The 1cR2PI mass resolved excitation spectra of the homo and eterochiral $\mathbf{E_R T_R}$ and $\mathbf{E_R T_S}$ clusters at m/e = 210 are reported in Figure 1. As already found in the clusters $\mathbf{P_R T_R}$ and $\mathbf{P_R T_S}$ [3] the excitation spectrum of $\mathbf{E_R T_R}$ is red shifted ($\Delta\nu = -101\ cm^{-1}$) relative to that of the bare chromophore, while the excitation spectrum of $\mathbf{E_R T_S}$ is characterized by a multiplet that is blue shifted relative to the band origin of the bare $\mathbf{E_R}$ ($\Delta\nu = +5\ cm^{-1}$). The different extent of the spectral shifts of these diastereomeric clusters reflects the combined effects of attractive (electrostatic and dispersive) and repulsive (steric) interactions on the HOMO and LUMO energies of $\mathbf{E_R solv}$, and indicates that steric factors play a different role, which reduce the effect of the attractive electrostatic and dispersive interaction. The remarkable similarity of the $\Delta(\Delta\nu)$ values of the aromatic alcohols with $\mathbf{B_S}$ and $\mathbf{B_R}$ (13 cm^{-1} for $\mathbf{P_R}$ and 12 cm^{-1} for $\mathbf{E_R}$) and with $\mathbf{A_S}$ and $\mathbf{A_R}$ (18 cm^{-1}) for $\mathbf{P_R}$ and 17 cm^{-1} for $\mathbf{E_R}$) indicates that the extent of chiral recognition is not significantly influenced by the interaction of the alkyl group (methyl or ethyl) of the chromophores with the **solv** [3, 5].

Figure 2 shows the 1cR2PI excitation spectra at

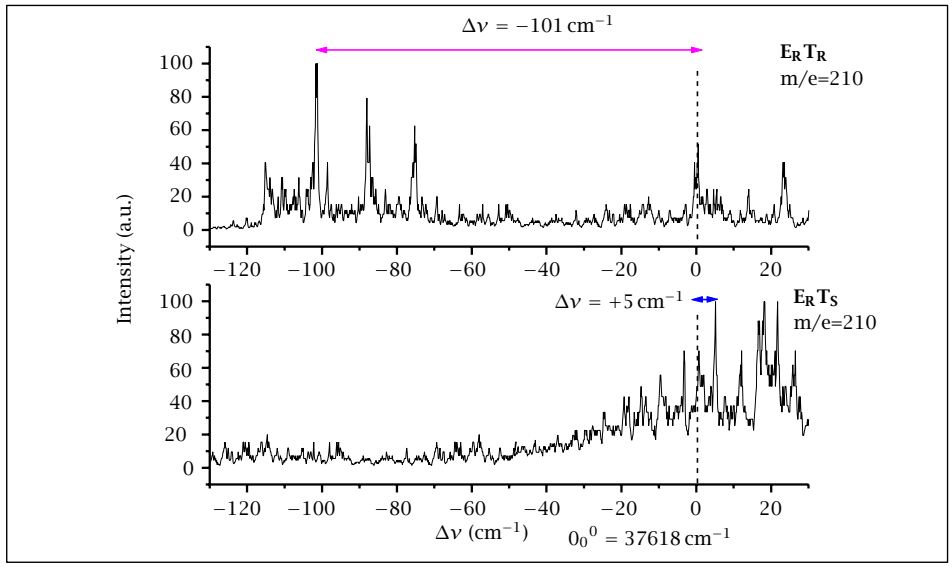

Figure 1. 1cR2PI *mass resolved excitation spectra of complexes between (+)-(R)-1-phenyl-ethanol (***$\mathbf{E_R}$***) and (a)* (−)*-(R)-2-pentanol (***$\mathbf{T_R}$***) and (b) (+)-(S)-2-pentanol (***$\mathbf{A_S}$***). The origin of the frequency scale is relative to the* $S_1 \leftarrow S_0$ *electronic band origin of bare* E_R.

m/e=195 of the homo and heterochiral $\mathbf{E_RA_R}$ (a), and $\mathbf{E_RA_S}$ (b) amine complexes. Also in this case a red shift relative to the band origin of the bare chromophore is observed. These shifts are larger than those found for the sec-butyl alcohols. The red shift of the $\mathbf{E_RA_S}$ heterochiral complex ($\Delta\nu = -161\,\mathrm{cm}^{-1}$) exceeds that of the homochiral one ($\Delta\nu = -144\,\mathrm{cm}^{-1}$) by $17\,\mathrm{cm}^{-1}$ in agreement with other cases [4].

In the 1cR2PI mass spectral patterns, strong signals at m/e= 74 ($[A_{R(S)}H]^+$), corresponding to the dissociative proton transfer (DPT), are observed. Intracluster reactivity between ionized aromatic molecules, as $\mathbf{P_R}$ [13] and 4-Fluorostyrene [14] and amines has been previously observed and appropriately related to the solute and the solvent ionization potentials and proton affinity (PA). It appears that, also in this case, the charged moiety transfers a proton to the 2-butylamine (PA=222 Kcal/mol). The homochiral adduct $\mathbf{E_RA_R}$ undergoes more fragmentation than the heterochiral one. This fact can be due to a higher probability of populating the dissociative states in $\mathbf{E_RA_R}$ clusters than in the heterochiral homologues.

The mass resolved 1cR2PI excitation spectrum of the bare $\mathbf{I_R}$ is reported in Figure 3 in a region about $800\,\mathrm{cm}^{-1}$ above the $S_1 \leftarrow S_0$ electronic origin. The band origin region of the spectrum displays two peaks at 37067 and $37183\,\mathrm{cm}^{-1}$. This pattern is by nomeans unusual and can be interpreted to be due either to vibrational frequencies or to the presence of two different stable conformers, where the OH is quasi axial or quasi equatorial respect to the aromatic ring as already hypotized by measuring the OH stretching frequencies of the molecules.

3.2.* 2cR2PI *ionization spectra and binding energies of molecular complexes. In Figure 4 the 2cR2PI ionization thresholds for E_RB_R (a) and $\mathbf{E_RB_S}$ (b) are shown. From the dissociative ionization threshold curves, binding energies D_0", for $\mathbf{E_RB_S}$ and $\mathbf{E_RB_R}$ of 3.7 ± 2.3 KJ/mol and 8.0 ± 2.3 KJ/mol are determined. Such low values may be ascribed to the difference between the experimental and adiabatic *IP* of $\mathbf{E_R}$. The binding energy difference (D_0"$(4.7 \pm 2.3$ KJ/mol) is consistent with the values measured for $\mathbf{P_RB_S}$ and $\mathbf{P_RB_R}$ ($\Delta D_0" = 4.6 \pm 1.7$ KJ/mol) [3].

4. CONCLUSIONS

The R2PI/TOF technique has been applied to investigate the nature of the forces acting in molecular complexes generated in a supersonic molecular beam. This technique is particularly valuable for spectroscopically discriminating diastereomeric clusters and for measuring their relative thermodynamic stability. It appears that there is a an interplay between the attractive and repulsive interactions in the ground and excited state clusters, which depends on the configuration of **solv** and on the structure of the chromophore **C**. It should be pointed out that the gaseous phase isolated homochiral complexes are more stable than the heterochiral ones.

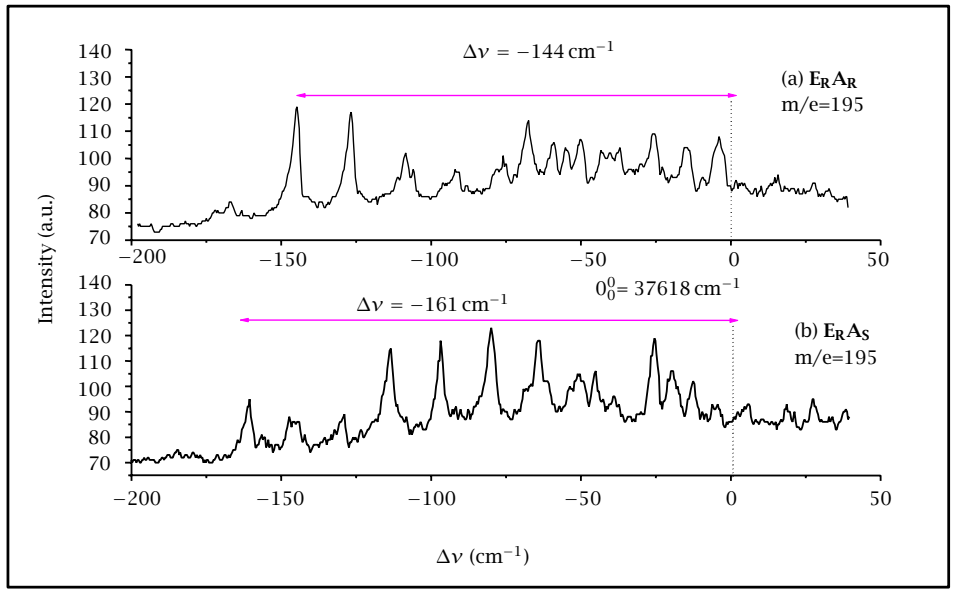

Figure 2. 1cR2PI *mass resolved excitation spectra of complexes between (+)-(R)-1-phenyl-ethanol (***$\mathbf{E_R}$***) and (a) (−)-(R)-2-butylamine (***$\mathbf{A_R}$***) and (b) (+)-(S)-2-butylamine (***$\mathbf{A_S}$***). The origin of the frequency scale is relative to the* $S_1 \leftarrow S_0$ *electronic band origin of bare* E_R.

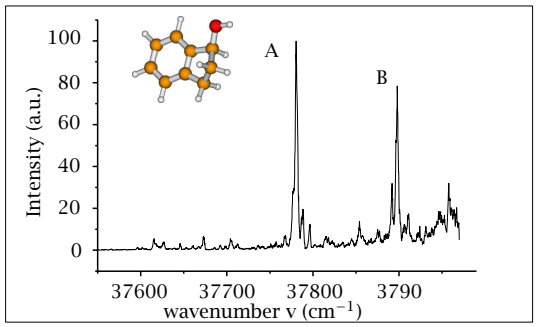

Figure 3. *Mass resolved* 1cR2PI *excitation spectrum of the bare chromophore (+)-(R)-1-indanol (*$\mathbf{I_R}$*), measured at m/e*=134 *at a total stagnation pressure of* 3×10^5 *Pa, and its structure.*

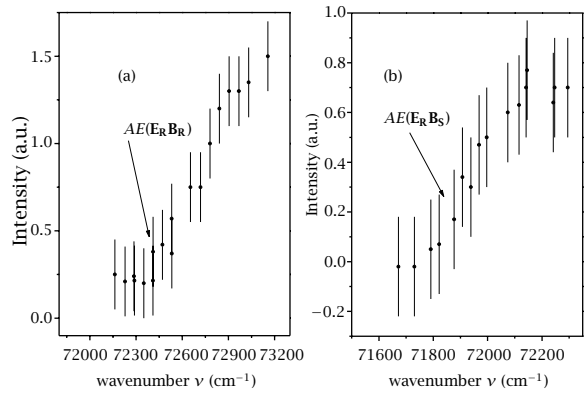

Figure 4. 1cR2PI *fragmentation thresholds (AE) of the complexes between (+)-(R)-*1*-phenyl-*1*-ethanol (*$\mathbf{E_R}$*) and (a) (−)-(R)-2-butanol (*$\mathbf{B_R}$*) and (b) (+)-(S)-2-butanol (*$\mathbf{B_S}$*). In case (a) the excitation wavenumber of the* ν_1 *photon is kept at* 37499 cm^{-1} $S_1 \leftarrow S_0$ *electronic transition of* $\mathbf{E_R B_R}$*, whereas in the case (b) the excitation wavenumber of the* ν_1 *photon is kept at* 37487 cm^{-1} $S_1 \leftarrow S_0$ *electronic transition of* $\mathbf{E_R B_S}$.

ACKNOWLEDGEMENT

The authors wish to acknowledge Prof. Aldo Mele and Prof. Robert Continetti for helpful discussions. This work was supported by the Ministero della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR) P.F. MSTAII.

References

[1] S. Piccirillo, C. Bosman, D. Toja, A. Giardini Guidoni, M. Pierini, A. Troiani, and M. Speranza, Angew. Chem. Int. Ed. Engl. **36** (1997), 1729.

[2] A. Latini, D. Toja, A. Giardini Guidoni, S. Piccirillo, and M. Speranza, Angew. Chem. **38** (1999), 815.

[3] A. Latini, M. Satta, A. Giardini Guidoni, S. Piccirillo, and M. Speranza, Chem. Eur. J. **6** (2000), 1042.

[4] A. Latini, D. Toja, A. Giardini Guidoni, A. Palleschi, S. Piccirillo, and M. Speranza, Chirality **11** (1999), 376.

[5] A. Giardini Guidoni, S. Picirillo, D.Scuderi, M. Satta,

T. M. Di Palma, and M. Speranza, Phys. Chem. Chem. Phys. **2** (2000), 4139.
[6] D. Consalvo, A. van der Avroid, S. Piccirillo, M. Coreno, A. Giardini Guidoni, A. Mele, and M. Snels, J. Chem. Phys. **99** (1993), 8398.
[7] Gaussian 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., *et al.*, Gaussian, Inc., Pittsburgh PA, 1998.
[8] L. P. Dovies, R. M. Guidry, J. R. Williams, M. J. Dewar, and H. S. Rzepa, J. Comp. Chem. **2** (1981), 433.
[9] Abdel Rahman Al Rabaa, PhD Thesis, Lab. Phot. Mol. Universite' de Paris Sud Orsay, 1997.
[10] A. Courty, M. Mons, I. Dimicoli, F. Piuzzi, M. P. Gaigeot, V. Brenner, P. de Pujo, and P. Millie, J. Phys. Chem. **102** (1998), 4890.
[11] W. Garret and T. S. Zwier, J. Chem. Phys. **96** (1992), 7259.
[12] M. R. Topp, Int. Rev. Phys. Chem. **12** (1993), 149.
[13] A. Giardini-Guidoni and S. Piccirillo, Israel J. of Chem. **37** (1997), 439.
[14] S. Piccirillo, M. Coreno, C. Bosman, A. Giardini Guidoni, A. Mele, and A. Palleschi, Chem. Phys. Lett. **247** (1995), 577.
[15] K. Hanaya, S. Onodera, Y. Ikegami, H. Kudo, and K. Shimaya, J. C. S. **Perkin II** (1980), 944.