[7] R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 791.
[8] a) N. E. Brese, M. O'Keefe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192; b) S. D. Waezsada, F.-Q. Liu, C. E. Barnes, H. W. Roesky, M. L. Montero, I. Usŏn, *Angew. Chem.* **1997**, *109*, 2738; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2625.
[9] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.
[10] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
[11] G. M. Sheldrick, SHELX 97, Universität Göttingen, Germany, **1997**.

Energetics of Molecular Complexes in a Supersonic Beam: A Novel Spectroscopic Tool for Enantiomeric Discrimination**

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Enantiomeric discrimination takes place when a chiral selector (C) forms with a pair of enantiomers (M) two diastereomeric molecular complexes (MCs) of different stability (thermodynamic enantioselectivity). This is the basis of chiral chromatography, enzymic resolution, asymmetric synthesis, and NMR spectroscopic discrimination with chiral auxiliaries.[1, 2] Although the principles of thermodynamic enantioselectivity find eminent applications in many fields, very few experiments have been designed so far to establish at the microscopic level the nature and energetics of the various interactions in diastereomeric MCs.

Thermometric measurements of the energetics of aggregation of chiral ions in solution to make diastereomeric ion pairs were first carried out by Arnett and Zingg.[3] These authors pointed out that the average difference in thermodynamic stability between diastereomeric combinations of several chiral amines with mandelic acid enantiomers may span from zero to 200 – 350 cal mol^{-1}, depending upon the structure of the amine and the nature of the solvent.

A way to evaluate the intrinsic nature of the various interactions in diastereomeric MCs and to eliminate the moderating effects of solvent on their energetics is to study their features in the isolated state. Here we report on the first spectroscopic determination of the binding energy in isolated diastereomeric MCs, with special regard to the dependence of the binding energy on the configuration of the chiral solvent molecule.

Weakly bound MCs, which would be unobservable at room temperature, can be readily generated in the isolated state by supersonic expansion of their components. Under these conditions, they are formed at an average temperature of a few Kelvins[4] and can be spectroscopically discriminated. The spectral analysis is facilitated by the fact that, at low temperatures, only the lowest rotational and vibrational levels are populated. Lahmani and co-workers recently characterized jet-cooled diastereomeric MCs by different laser-induced fluorescence (LIF) spectra.[5–7] Discrimination between diastereomeric MCs was obtained by us[8] with resonance-enhanced multiphoton ionization (REMPI) spectroscopy combined with time-of-flight (TOF) mass spectrometry.[4, 9] Accordingly, the REMPI-TOF spectra of the diastereomeric molecular complexes **Rr** and **Rs**—formed from the combination of the chiral chromophore (*R*)-(+)-1-phenyl-1-propanol (**R**) with (*R*)-(−) (**r**) and (*S*)-(+)-2-butanol (**s**), respectively—display different features. In particular, their most intense band, assigned to the electronic band origin, is red-shifted relative to the $S_1 \leftarrow S_0$ band origin of the isolated **R** molecule ($\Delta\nu = -79$ cm^{-1} (**Rr**), -92 cm^{-1} (**Rs**)), indicating an enhancement of binding energy of both **Rr** and **Rs** adducts in the S_1 state relative to the S_0 state. The difference between the red shifts ($\Delta\nu[\mathbf{Rr}] - \Delta\nu[\mathbf{Rs}] = 13$ cm^{-1}) reflects a $S_1 \leftarrow S_0$ energy gap for **Rs** which is smaller than for **Rr**.

The binding energy of the diastereomeric **Rr** and **Rs** adducts was measured by two color resonance two photon ionization (2cR2PI) experiments. The species under investigation is selectively excited to the S_1 state by absorption of one photon at a fixed frequency ν_1 ($h\nu_1$ in Figure 1), and then ionized by a second photon of variable frequency ν_2 ($h\nu_2$ in Figure 1). The experimental procedure is the following: the species under unvestigation was first submitted to one color resonance two photon ionization (1cR2PI) experiments,[8] in which it is excited to a discrete S_1 state by absorption of one photon of frequency ν_1, and to the ionization continuum by absorption of another photon with the same frequency ν_1. Once having obtained the 1cR2PI-TOF mass spectrum of the selected species at the resonance frequency ν_1, the intensity of the laser emitting at ν_1 is lowered so as to reduce the TOF ion pattern to less than 10%. Then, by superimposing a second laser of variable frequency ν_2, which alone does not produce any significant signal in the spectral region of interest, there is a pronounced increase in the intensity of the TOF signal of a characteristic ion only when the 2cR2PI process takes place. The value of ν_2 corresponding to the signal onset provides a measure of the ionization threshold of the species.

The energetics involved in diastereomeric **Rr** or **Rs** is determined as follows: The dissociation energy D_0'' of ground-state **Rr** is computed from Equation (1), namely, from the difference between its dissociative ionization threshold ($h\nu_1[\mathbf{Rr}^*] + h\nu_2[\mathbf{R}^+ + \mathbf{r}]$; Figure 1) and the ionization threshold of bare **R** ($\mathrm{IP}(\mathbf{R}) = h\nu_1[\mathbf{R}^*] + h\nu_2[\mathbf{R}^+]$). The dissociation energy D_0^+ of ionic cluster $\mathbf{Rr}^+$ is calculated from Equation (2), namely, from the difference between its dissociative ionization threshold ($h\nu_1[\mathbf{Rr}^*] + h\nu_2[\mathbf{R}^+ + \mathbf{r}]$; Figure 1) and its

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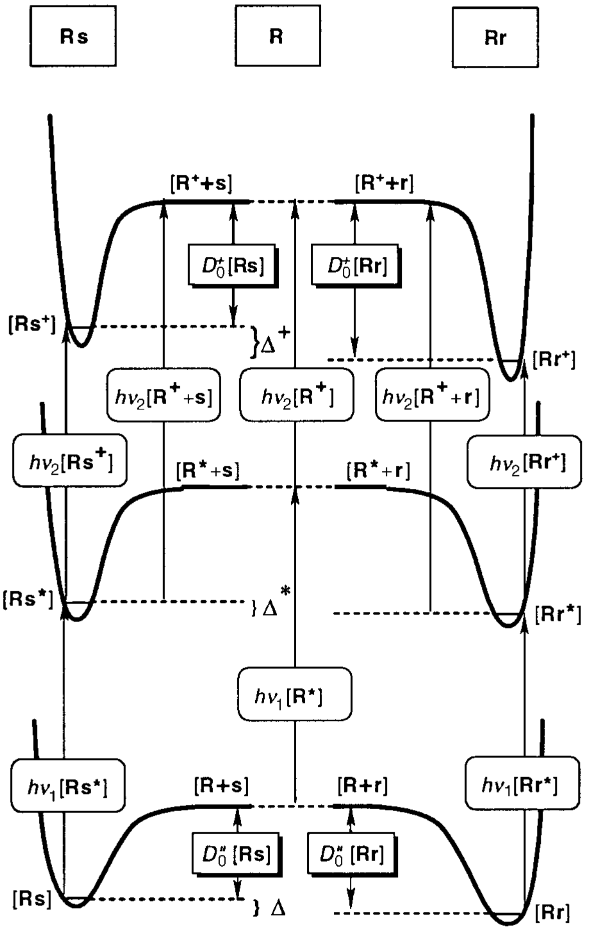

Figure 1. Schematic representation of the potential energy curves for the heterochiral complex **Rs** (left) and the homochiral complex **Rr** (right). The arrows on the center of the diagram refer to the bare chromophore **R**. Excitation ([**Rs***] and [**Rr***]), ionization ([**Rs**$^+$] and [**Rr**$^+$]), and dissociative ionization energies ([**R**$^+$ + **s**] and[**R**$^+$ + **r**]) are reported in Table 1. The terms Δ, Δ*, and Δ$^+$ refer to the experimental energy gap between **Rr** and **Rs** in their ground, first excited, and ionized state, respectively.

ionization threshold (IP(**Rr**) = $h\nu_1$[**Rr***] + $h\nu_2$[**Rr**$^+$]). Of course, similar equations can be derived for the heterochiral complex **Rs**.

$$D_0'' = h\nu_1[\mathbf{Rr}^*] + h\nu_2[\mathbf{R}^+ + \mathbf{r}] - \mathrm{IP}(\mathbf{R}) \quad (1)$$

$$D_0^+ = h\nu_1[\mathbf{Rr}^*] + h\nu_2[\mathbf{R}^+ + \mathbf{r}] - \mathrm{IP}(\mathbf{Rr}) = h\nu_2[\mathbf{R}^+ + \mathbf{r}] - h\nu_2[\mathbf{Rr}^+] \quad (2)$$

The band-origin region of the mass-resolved 2cR2PI excitation spectrum of bare **R** is characterized by a peak at 37577 cm^{-1} and two other major peaks at 37618 and 37624 cm^{-1}. By analogy with the spectral features of similar molecules,[10, 11] this triplet of bands can be interpreted as being due to either different stable conformers or vibronic transitions. We tend to support the first hypothesis since analysis of the excitation spectrum around 530 cm^{-1} above the electronic $S_0 \leftarrow S_1$ origin reveals the presence of a mirror triplet at 38106, 38148, and 38155 cm^{-1}. These vibronic bands around 530 cm^{-1} above the electronic $S_0 \leftarrow S_1$ origin ($6b_0^1$) characterize the spectrum of many substituted benzenes and are independent of the nature of the substituent.[11]

The 2cR2PI ionization spectrum of bare **R** is taken by setting ν_1 at a value corresponding to any of the bands between 37577 and 37624 cm^{-1} and by varying ν_2. All these measurements provide the same value for the appearance potential of **R**$^+$ (8.84 eV) within the limits of experimental uncertainty (±0.01 eV).

The 2cR2PI ionization spectra and dissociative ionization spectra of the diastereomeric pair **Rr** and **Rs** are taken in the same way, by setting ν_1 at a value corresponding to their band origin. Figure 2 displays the 2cR2PI ionization spectrum and dissociative ionization spectrum of the **Rr** complex. Similar spectra are obtained for the other diastereomer **Rs**. The appearance potential and dissociative appearance potential of **Rr** and **Rs** are listed in Table 1, together with their derived D_0'' and D_0^+ dissociation energies. The D_0'' values demonstrate that the homochiral **Rr** complex is appreciably more stable toward dissociation than the heterochiral **Rs** adduct. This trend extends to the S_1 excited complexes as well, that is, $\Delta^* = D_0''[\mathbf{Rr}^*] - D_0''[\mathbf{Rs}^*] = \Delta - 13\ \mathrm{cm}^{-1} = 1.1 \pm 0.4\ \mathrm{kcal\,mol}^{-1}$ (Figure 1).

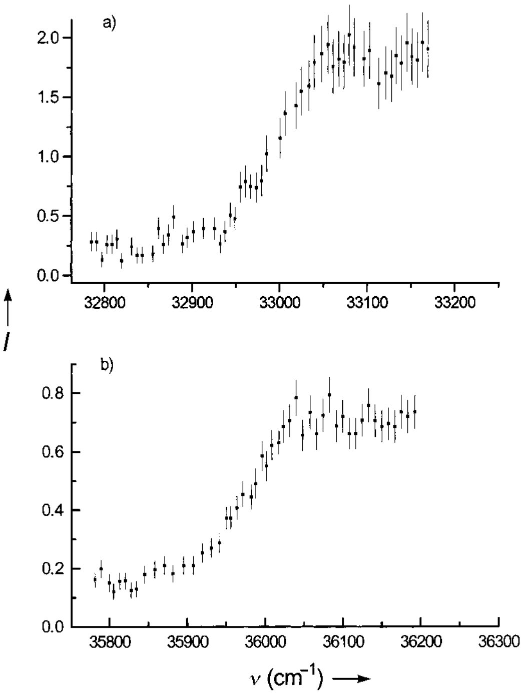

Figure 2. a) The 2cR2PI ionization spectrum and b) the dissociative ionization spectrum of the complex **Rr** at a threshold of m/z 210 and a total stagnation pressure of 4×10^5 Pa. Intensity I is given in arbitrary units.

Table 1. Photon energies for excitation, threshold ionization, and threshold dissociative ionization of the **Ra** (**a** = **s** or **r**) complexes and their derived binding energies in the neutral (D_0'') and cationic ground state (D_0^+); see also Figure 1.

	$h\nu_1$[**Ra***] [cm^{-1}]	$h\nu_2$[**Ra**$^+$] [cm^{-1}]	$h\nu_2$[**R**$^+$ + **a**] [cm^{-1}]	D_0''[a] [kcal mol^{-1}]	D_0^+[b] [kcal mol^{-1}]
Rr	37498 ± 1	32950 ± 40	35890 ± 40	5.9 ± 0.2	8.4 ± 0.2
Rs	37485 ± 1	33160 ± 40	35540 ± 40	4.8 ± 0.2	6.8 ± 0.2
				Δ = 1.1 ± 0.4	Δ$^+$ = 1.6 ± 0.4

[a] D_0'' as derived from Equation (1) (IP(**R**) = 8.84 ± 0.01 eV). [b] D_0^+ as derived from Equation (2).

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The measured difference in red shifts of $\Delta - \Delta^* = 13\ \mathrm{cm^{-1}}$ for **Rr** and **Rs** indicates that the interaction energies in these MCs respond to a complicate interplay of steric effects and dispersive forces. In fact, the red shifts reflect the strengthening of the dispersion (polarization and charge transfer) forces in the corresponding excited adducts. However, the observation that the larger red shift is associated with the less stable complex **Rs** (Table 1) indicates a dual effect of the HOMO →LUMO electron transition in the chromophoric moiety of **Rr** and **Rs**. This not only enhances the attractive dispersion forces, but also alters to a different extent the repulsive forces arising from steric congestion in the complexes.

The values for D_0^+ in Table 1 qualitatively parallel the corresponding D_0'' energies. The homochiral complex $\mathbf{Rr}^+$ is more stable toward dissociation than the heterochiral adduct $\mathbf{Rs}^+$. However, comparison of $\Delta = 1.1 \pm 0.4\ \mathrm{kcal\,mol^{-1}}$ and $\Delta^+ = 1.6 \pm 0.4\ \mathrm{kcal\,mol^{-1}}$ reveals that extra stabilization due to ionization is larger for the more stable homochiral complex **Rr** (Table 1). These findings are consistent with the hypothesis of a homochiral complex **Rr**, wherein steric hindrance between the two moieties is less demanding, and therefore tightening between them after chromophore ionization is easier.

In conclusion, the 2cR2PI/TOF technique has been applied for the first time to measure the energetics of neutral and ionic diastereomeric complexes between a chiral aromatic alcohol and a chiral aliphatic alcohol in a supersonic beam. The homochiral **Rr** complex is more stable than the heterochiral **Rs** diastereomer in both the ground and excited states. The same is true for the corresponding ionic adducts. The difference in stability for the neutral adducts is attributed to different steric requirements.

Experimental Section

The experimental setup for the generation of MCs and their spectral analysis was described previously.[8] Supersonic beam production of the MCs was obtained by adiabatic expansion of a carrier gas (Ar), seeded with the corresponding alcohols **R** and **r** or **s** (Aldrich Chemical Co.), through a pulsed 400-μm nozzle kept at 85 °C. The molecular beam was allowed to pass through a 1-mm skimmer into a second chamber equipped with a TOF spectrometer. The laser system consisted of a Nd:YAG doubled in frequency ($\lambda = 532$ nm) which pumps two dye lasers. The dye frequencies were doubled and, when necessary, mixed with residual 1064-nm radiation. The ions formed by 2cR2PI ionization in the TOF source are mass-discriminated and detected by a channeltron after a 50-cm flight path. The photoionization results are corrected for the effect of the electric field strength ($200\ \mathrm{V\,cm^{-1}}$) produced by the extraction plates of the TOF spectrometer.

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[1] W. H. Pirkle, T. G. Pochapsky, *Chem. Rev.* **1989**, *89*, 347.

[2] D. Parker, *Chem. Rev.* **1991**, *91*, 1441.

[3] E. M. Arnett, S. P. Zingg, *J. Am. Chem. Soc.* **1981**, *103*, 1221.

[4] a) N. Ramsey, *Molecular Beams*, Oxford Clarendon, Oxford, **1956**; b) R. E. Smalley, B. L. Ramakrishna, D. H. Levy, L. Wharton, *J. Chem. Phys.* **1974**, *61*, 4363; c) S. Piccirillo, M. Coreno, A. Giardini-Guidoni, G. Pizzella, M. Snels, R. Teghil, *J. Mol. Struct.* **1993**, *293*, 197; d) M. Coreno, S. Piccirillo, A. Giardini Guidoni, A. Mele, A. Palleschi, P. Brechignac, P. Parneix, *Chem. Phys. Lett.* **1995**, *236*, 580; e) T. M. Di Palma, A. Latini, M. Satta, M. Varvesi, A. Giardini Guidoni, *Chem. Phys. Lett.* **1998**, *284*, 184.

[5] R. R. Al-Rabaa, E. Bréhéret, F. Lahmani, A. Zehnacker-Rentien, *Chem. Phys. Lett.* **1995**, *237*, 480.

[6] R. R. Al-Rabaa, K. Le Barbu, F. Lahmani, A. Zehnacker-Rentien, *J. Phys. Chem.* **1997**, *101*, 3273.

[7] K. Le Barbu, V. Brenner, P. Millié, F. Lahmani, A. Zehnacker-Rentien, *J. Phys. Chem. A* **1998**, *102*, 128.

[8] S. Piccirillo, C. Bosman, D. Toja, A. Giardini-Guidoni, M. Pierini, A. Troiani, M. Speranza, *Angew. Chem.* **1997**, *109*, 1816; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1729.

[9] a) W. C. Wiley, I. H. McLaren, *Rev. Sci. Instrum.* **1955**, *26*, 1150; b) B. Brutschy, *Chem. Rev.* **1992**, *92*, 1567.

[10] a) S. Sun, E. R. Bernstein, *J. Am. Chem. Soc.* **1996**, *118*, 5086; b) S. Li, E. R. Bernstein, *J. Chem. Phys.* **1992**, *97*, 7383.

[11] a) J. B. Hopkins, D. E. Powers, S. Mukamel, R. E. Smalley, *J. Chem. Phys.* **1980**, *72*, 5049; b) J. B. Hopkins, B. E. Powers, R. E. Smalley, *J. Chem. Phys.* **1980**, *72*, 5039.

Monodisperse Poly(triacetylene) Rods: Synthesis of a 11.9 nm Long Molecular Wire and Direct Determination of the Effective Conjugation Length by UV/Vis and Raman Spectroscopies**

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François Diederich*

*Dedicated to Professor Armin de Meijere
on the occasion of his 60th birthday*

The study of oligomers with precisely defined length and constitution has become an important tool for providing specific information concerning the structural, electronic, and optical properties of the corresponding polydisperse, long-chain polymeric analogues.[1, 2] A second interest in monodisperse, π-conjugated rod-like oligomers arises from their potential to function as molecular wires in molecular scale electronics and nanotechnological devices.[3] Recently, we described the synthesis of a series of monodisperse $\mathrm{Me_3Si}$-endcapped poly(triacetylene) oligomers (PTA oligomers) that ranged from a 0.96 nm long monomeric to a 4.61 nm long hexameric rod.[4] By extrapolative evaluation of linear optical and third-order nonlinear optical data we predicted an effective conjugation length (ECL) in the range of 7 to 10 monomer units for poly(triacetylenes). The ECL[5, 6] defines the number of repeat or monomer units in a π-conjugated

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