van der Waals Complexes between Chiral Molecules in a Supersonic Jet: A New Spectroscopic Method for Enantiomeric Discrimination

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van der Waals complexation in a supersonic expansion combined with laser-induced fluorescence techniques have been used to discriminate between isolated diastereoisomer pairs of weakly bound species. By using 2-naphthyl-1-ethanol (2-NetOH) as the chiral chromophore, we have investigated the effect of complexation with different aliphatic alcohols on the microscopic shifts of the S_0-S_1 transition and on the fluorescence decay times of the chromophore. The fluorescence excitation spectra of the complexes of 2-NetOH with nonchiral primary alcohols have been first examined, and the binding energy of the complex of 2-NetOH with methanol has been determined to be on the order of 1000 cm^{-1}. In the case of complexation with chiral solvents such as 2-methyl-1-butanol or secondary alcohols, the homochiral and heterochiral pairs give rise to specific spectral shifts and patterns which allow them to be clearly distinguished. The fluorescence lifetimes following excitation of alcoholic complexes in every case are longer than those of the uncomplexed chromophore and also depend on the particular diastereoisomer excited. The chiral recognition evidenced on the spectral properties and on the dynamical relaxation processes of isolated enantiomeric pairs shows the nonequivalence of their interaction energy in both the ground and excited states. The nature of the stereochemically dependent interactions can be tentatively described on the grounds of a hydrogen bonded intermolecular structure involving a folded geometry of the alkyl chain with respect to the naphthalene nucleus.

Introduction

Chirality dependent molecular interactions and chiral recognition in chemical and physical processes are of fundamental importance in chemistry and biology. The enantioselective behavior of many natural systems observed in enzymatic reactions or drug activity is usually described in terms of the intermolecular contact pairs in a lock and key arrangement and the stereochemical factors which govern their interactions. Discrimination of optical isomers requires an external agent that is chiral by itself to be able to recognize their handedness by interacting in a different way with the *R* or *S* form. Besides the chirooptical methods which involve circularly polarized light such as circular dichroism, other widely used techniques need the presence of a chiral agent or medium to convert the mixture of enantiomers into diastereoisomers. The principle of diastereoisomerism provides the basic mechanism for chromatographic separation of enantiomers on chiral stationary phases[1] and of NMR techniques using a chiral auxiliary such as lanthanide reagents or chiral solvating agents.[2] Although the basic concept of enantioselectivity resting on the nonequivalence of *R*−*R* and *R*−*S* diastereoisomers as a consequence of different interaction energy has been applied for a long time in these chemical analytic methods, there are very few experiments designed to get more accurate information on the nature of the various interactions between chiral partners and on the differential energy which contributes to the chiral discrimination at the microscopic level.

We have recently shown that chiral discrimination can be achieved by producing diastereoisomeric van der Waals complexes of a chiral chromophore with a chiral solvent in a supersonic expansion.[3] The supersonic expansion cools down the internal degrees of freedom of the compounds under study and generates weakly bound complexes that would have been unstable at room temperature. In these conditions, different isomeric pairs associated with different local minima of the potential energy surface can coexist in the cold region of the jet. This phenomenon is well documented in many cases of van der Waals complexes or clusters and has been evidenced in systems such as aromatic dimers,[4] clusters of aromatic molecules with several argon atoms,[5] and complexes involving partners with several conformations or complexation sites.[6,7] Because of the low internal temperature of the molecules, weakly bound diastereoisomers with slightly different heats of formation and a large barrier for racemization are not expected to interconvert and thus can be considered as a particular class of isomers that can be trapped out and subsequently probed in the supersonic jet. Furthermore, at these low temperatures, the electronic transitions become sharp and well resolved and in the case of complexation with a fluorescent chromophore, the two diasterereoisomer pairs can be probed by laser-induced fluorescence spectroscopy in the region of the electronic origin of the S_0-S_1 transition of the chromophore. Complexation usually results in the appearance of new features in the fluorescence excitation spectrum that are displaced with respect to the noncomplexed chromophore (microscopic solvent shift). Different microscopic solvent shifts are thus expected for the homochiral and heterochiral pairs. In our preliminary study,[3] we have used 2-naphthyl-1-ethanol (2-NetOH) as the chromophore and (*S*)-2-chloro-1-propanol as the complexing agent and we have shown indeed that the *R*−*S* an *S*−*S* complexes lead to different microscopic shift. In the present work we have performed a more systematic investigation of the spectroscopic properties of van der Waals complexes of 2-NetOH with a series of alcohols. In the first part of the paper the complexation with nonchiral alcohols has been studied in order to get a more general picture of the nature and energetics of the intermolecular forces acting in these systems. Two points were examined more precisely, the first of which deals with the effect of the nature

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of the alcoholic complexing solvent on the spectral characteristics of the clusters (influence of the alkyl chain length with a special attention paid to the possibility of different conformations and to the role of the relative acidity of the alcoholic solvent with respect to the 2-NetOH chromophore). The second point was devoted to the experimental determination of the bonding energy between 2-NetOH and methanol which can be considered as a prototype for these systems. In the second part of the paper, complexes of 2-NetOH with chiral alcohols such as 2-methyl-1-butanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-octanol were investigated in order to assess the generality of our method using spectroscopic determination of the microscopic shift of the S_0-S_1 transition in jet cooled cooled conditions for chiral discrimination.

Experimental Section

The method used in these experiments combines a supersonic jet and laser induced fluorescence measurements. The supersonic free jet was produced by expanding a continuous flow of helium at a pressure of 2 atm in a vacuum chamber maintained at 10^{-3} Torr through a 200 μm nozzle. The helium carrier gas is seeded by mixing a helium flow saturated with the solvent with a second flow passing over the 2-naphthyl-1-ethanol sample contained in a small oven just before the nozzle and heated to ~70 °C in order to achieve enough vapor pressure. The bare chromophore and complexes are excited by means of a frequency-doubled dye laser pumped by the second harmonic of a 10 Hz pulsed YAG laser and aligned perpendicularly to the beam axis. The emitted fluorescence is collected at right angles to both the excitation laser pulse and the beam axis through collecting lenses and recorded either globally through a WG 335 Schott filter for elimination of the scattered laser light or after dispersion through a 60 cm Jobin Yvon monochromator by a Hammamatsu R2059 photomultipler and subsequent electronics. The fluorescence decay times were measured with a 125 Mhz oscilloscope (Lecroy 9400). The laser pulse width is 10 ns and the rise time of the photomultiplier less than 3 ns.

The products in their racemic or optically resolved forms were obtained from Aldrich and used as supplied.

Results and Discussion

(A) Complexes of 2-Naphthyl-1-ethanol with Nonchiral Primary Alcohols. *Fluorescence Excitation Spectra.* The laser-induced fluorescence excitation spectrum of bare 2-naphthyl-1-ethanol (2-NetOH) has been reported previously.[3] Its 0−0 transition located at 31738.4 cm^{-1} is followed by two low-frequency features at 39 and 76 cm^{-1} assigned to torsional motion of the $CH(CH_3)-OH$ group by analogy with 2-ethylnaphthalene[8] and benzyl alcohol[9] where similar low-frequency modes are observed. We have also shown that complexation of 2-NetOH with methanol gives rise very easily to strongly fluorescent, slightly red-shifted clusters. The fluorescence excitation spectra of mixtures of 2-NetOH with other linear primary alcohols (ethanol, *n*-propanol, *n*-butanol, and 2,2,2-trifluoroethanol) are presented on Figure 1. As shown on Figure 1, the formation of complexes is evidenced by the appearance of new features and comparison of the spectra indicates some common trends.

(i) The origin bands are red shifted with respect to the monomer 0−0 transition for the series ethanol, *n*-propanol, and *n*-butanol while the complex with trifluoroethanol is blue shifted (Table 1). The complexes under study consist of two alcohols, and the intermolecular forces present should involve an hydrogen bond between the two partners. In the case of complexation with alkyl primary alcohol, the 2-NetOH molecule is expected to be the hydrogen bond donor since it is known from acidity studies[10] that aromatic and or secondary alcohols are stronger acids in the gas phase than primary alcohols. A microscopic solvent shift toward the low energy side is usually obtained in this situation as observed here. The substitution with fluorine atoms in the 2-position of ethanol is known to increase the hydrogen bond donor character of this solvent due to the inductive substituent effect.[11] Thus the blue shift observed by complexation with trifluoroethanol probably reflects the fact that in this latter case the oxygen atom of the 2-NetOH chromophore is the site for accepting the hydrogen bond from the more acidic OH group of trifluoroethanol.[12]

(ii) The general pattern of the spectra in the red of the 0−0 transition shows that the most intense feature which is approximately at the same position for the series of normal alkyl alcohols is preceded toward the low energy side by less intense bands. This is an indication of the presence of several isomers or higher clusters. To distinguish the possible formation of higher clusters, the dependence of the main features intensity

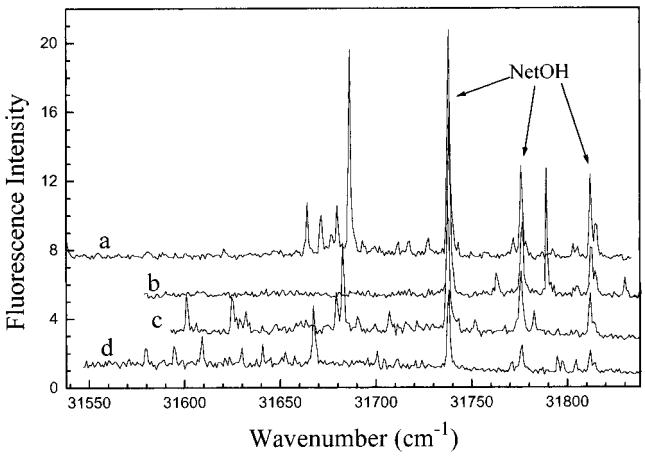

Figure 1. Fluorescence excitation spectra of 2-NetOH primary alcohols mixtures in a supersonic jet in the region of the origin of the S_0-S_1 transition: (a) ethanol, (b) trifluoroethanol, (c) *n*-propanol, (d) *n*-butanol. The bands corresponding to the bare chromophore are shown on the figure.

TABLE 1: Shifts and Fluorescence Decay Times of the Main Bands of Complexes of 2-NetOH with Primary Alcohols Relative to the Origin of the Bare Molecule S_0-S_1 Transition at 31 738 cm^{-1}

complexing alcohol	shift (cm^{-1})	lifetime (ns)
methanol (ref 3)	−67	33
	−55	160
	−43	151
ethanol	−61	63
	−55	
	−52	126
trifluoroethanol	+24	84
	+51	158
n-propanol	−138	119
	−112	54
	−60	55
	−55	119
n-butanol	−158	112
	−144	
	−125	
	−71	125
2-methyl-1-butanol (*R*−*S*)	−84	135
	−51	
	−34	
	−19	
2-methyl-1-butanol (*S*−*S*)	−134	140
	−118	
	−62	123
	+54	

as a function of the partial pressure of the solvent was studied. For the ethanol complexes, three bands are observed slightly to the red of the main feature. The first two bands are assigned to a 1:2 complex while the third one depends linearly on the partial pressure of ethanol and can be attributed to a 1:1 complex. For *n*-propanol and *n*-butanol complexes, the main spectral features exhibit the same linear pressure dependence and are therefore attributed to 1:1 complexes. The peculiar intensity distribution observed in these complexes seems thus to indicate the coexistence of at least two isomers. *n*-Propanol is known to take in the vapor phase both the anti and gauche conformations (with a slight enthalpy difference in favor of the gauche form) which may give rise to two different species. Such behavior is also expected in larger alcohols. Furthermore, the complexes involving only one conformation of the partners can take different geometrical arrangements and result also in different ground state isomers.

(iii) The low-frequency progression observed in the spectrum of the bare molecule is no longer apparent for the methanol and ethanol complexes. In the case of *n*-propanol and *n*-butanol, low-frequency bands appear for the most red systems. These structures are more likely to be due to an intermolecular van der Waals vibration.

Lifetimes. It has been observed in the previous paper[3] that complexation with methanol induces a dramatic lengthening of the fluorescence decay time of the 2-NetOH chromophore. The fluorescence decaytimes obtained for the excitation of the main bands of the 2-NetOH complexes with the other primary alcohols are reported in Table 1. It shows that the most intense bands observed in the spectra exhibit a long fluorescence lifetime with respect to the bare molecule origin (45 ns). However some features have also a short decay and the variation of the lifetimes does not appear to present a monotonous decrease as a function of energy as could be expected but changes somewhat erratically from one level to another.

This effect has already been observed in van der Waals complexes of other naphthalene compounds[13,14] and may be due either to a change of the radiative lifetimes or to the decrease of the intersystem-crossing rate constant induced by complexation. In a previously reported example,[14] the comparison of fluorescence excitation spectra with that of the sensitized phosphorescence produced by trapping the long-lived triplet molecules on a cooled surface has shown that the decrease of intersystem-crossing rate constant induced by complexation is responsible for the lengthening of the fluorescence decay. This unexpected behavior has been attributed to the detuning of an accidental resonance of the bare molecules singlet levels with a higher triplet state.

(B) Binding energy in the 2-Naphthyl-1-ethanol/Methanol Complex. It is interesting to evaluate quantitatively the ground state stabilization energy involved in the van der Waals complexation of 2-NetOH with the alcoholic solvents used in these experiments. We have thus performed an experimental determination of the binding energy by searching the dissociation threshold of the complex formed between 2-NetOH and methanol. The reason for this choice is that this complex is strongly fluorescent, and its absorption features can be evidenced at higher excitation energy. This is not usually straightforward in weakly absorbing complexes, since at higher excitation energy the fluorescence excitation spectrum becomes more and more congested and less intense because of competing nonradiative processes even for the bare molecule, and the bands belonging to the complex are difficult to identify.

The principle of the experiment rests on the observation of the appearance of the free 2-NetOH fluorescent fragment in the

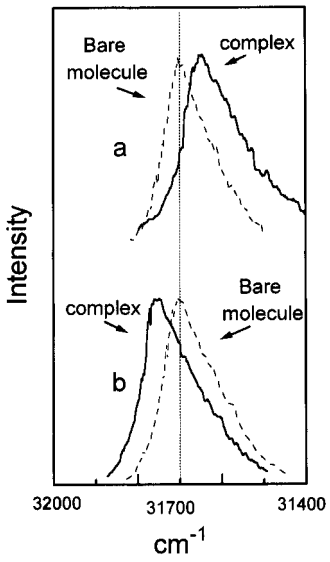

Figure 2. Comparison of the $\Delta v = 0$ emission band (a) for pure 2-NetOH excited in the 548 cm^{-1} vibrational band and its complex with methanol excited at 705 cm^{-1} above its origin and (b) for pure 2-NetOH excited in the 981 cm^{-1} vibrational level and its complex with methanol excited at 1060 cm^{-1} above its origin. The light lines correspond to the 2-NetOH excitation and the bold lines correspond to the complex. The widths ($\Delta\nu$ = 150 cm^{-1}) are determined by the monochromator resolution.

$v' = 0$ state as a function of the excitation energy. The fluorescence from 2-NetOH fragment arising from the predissociation of the complex can be distinguished from that of the bare molecule because, since it is produced at the threshold without excess vibrational energy, it presents a resonant fluorescence band located exactly on the 0−0 transition. In contrast, the excitation of the bare molecule in high vibronic levels results in a dispersed fluorescence spectrum broadened by intramolecular vibrational redistribution (IVR). Its first emission band corresponds to the $\Delta v = 0$ transitions arising from the numerous levels populated by IVR and is usually red shifted with respect to the resonant 0−0 transition.

This situation is illustrated on Figure 2. The Figure 2a displays the $\Delta v = 0$ emission band obtained for excitation of the bare molecule in the 548 cm^{-1} vibrational level and of the complex at 705 cm^{-1} excess vibrational energy above the origin of the S_0-S_1 transition. In both cases, because of intramolecular vibrational redistribution, these bands are lower in energy by ~40 cm^{-1} than the respective resonant 0−0 transitions. Furthermore, because of the shift induced by the complexation, the $\Delta v = 0$ emission band of the complex is located at ~60 cm^{-1} to the red of the corresponding band of the bare molecule. The dispersed fluorescence spectrum in the region of the 0−0 transition, following the excitation of the complex and the bare molecule excited with ~1000 cm^{-1} excess energy, is presented in Figure 2b. While the $\Delta v = 0$ fluorescence band originating from the bare molecule excitation is observed at the same energy as previously, the analogous band for the methanol complex is shifted toward the blue and peaks at 31 740 cm^{-1}, which corresponds to the 0−0 transition of the monomer.

This result shows that for this excess energy the complex is predissociated since the emitting species is the excited chromophore fragment. The energy threshold for production of the excited free NetOH from the complex is thus $700 < E < 1050$ cm^{-1}, indicating that the binding energy in the van der Waals complex is contained in this limit.

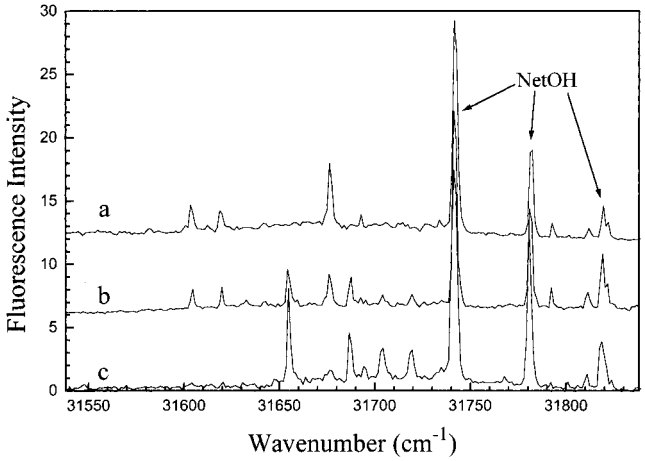

Figure 3. Fluorescence excitation spectra showing chiral discrimination in the jet-cooled complexes of 2-NetOH with 2-methyl-1-butanol used (a) in their *S*−*S* enantiomeric, (b) *R* racemic, and (c) *R*−*S* enantiomeric forms respectively.

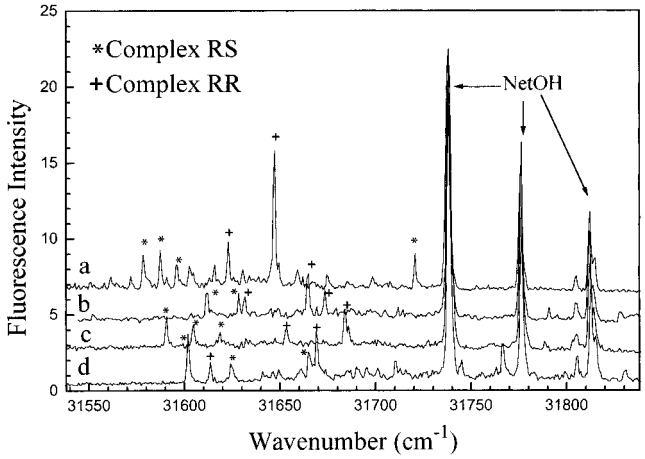

Figure 4. Fluorescence excitation spectra of mixtures of 2-NetOH with secondary alcohols (a) 2-octanol, (b) 2-hexanol, (c) 2-pentanol, and (d) 2-butanol. The bands corresponding to the bare chromophore are shown on the figure. The main features originating from the heterochiral pair are labeled with *, those from the homochiral pair by +.

An interaction energy of ∼1000 cm^{-1} (2.85 kcal mol^{-1}) is usual for van der Waals complexes between polyatomic molecules. Furthermore, in the system under study composed of two alcohols, it is expected that hydrogen bond involving the OH groups at the stereogenic center should participate to the binding energy. The binding energy in the dimer of methanol[15] has been measured to be ∼1034 cm^{-1} and compares well with the present determination.

(C) Complexes of 2-Naphthyl-1-ethanol with Chiral 2-Methyl-1-butanol. When (*S*)-2-methyl-1-butanol is added to the *S*- or (*R*)-2-NetOH sample, new features which can be assigned to the formation of van der Waals complexes appear on the low energy side of the transition of the bare molecule as shown on Figures 3a,c. From these spectra it can be immediately seen that the two diastereoisomeric complexes *S*−*S* and *R*−*S* exhibit at origin different solvent shifts and patterns which allow one to distinguish clearly between them.

In the case of the of the *S*−*S* association, the spectrum consists of two weak features shifted, respectively, by 131 and 117 cm^{-1}, and a third more intense band at 62 cm^{-1} shifted to the red of the origin of the bare molecule. Increasing the partial pressure of the 2-methyl-1-butanol solvent does not change the relative intensity of the weak bands at −131 and −117 cm^{-1} with respect to the more intense band at −62 cm^{-1}. The overall spectrum shows a linear variation as a function of the solvent concentration, indicating that it corresponds to a 1:1 stoichiometry. It is worth noticing that this spectrum bears a strong resemblance to the complex with *n*-propanol or *n*-butanol (Figure 1) indicating that the same kind of interactions are involved. As discussed before, the excitation spectra of both *n*-propanol and *n*-butanol display a strong band at ∼70 cm^{-1} from the bare molecule in addition to weak features shifted further to the red. This observation is difficult to rationalize in terms of a single structural species for the complex but suggests that two different conformational isomers of the complexes are present in the jet. A similar behavior seems to hold in the *S*−*S* association of 2-NetOH with (*S*)-2-methyl-1-butanol.

The *R*−*S* complex (Figure 3c) displays a different pattern with a strong 0−0 transition at −82 cm^{-1} from that of the bare molecule followed by a weaker system of three bands. This vibrational pattern indicates a significant activity in low-frequency modes. However, this spectrum may also contain features originating from different structural isomers.

The spectrum of Figure 3b has been obtained with the *R* enantiomer of the chromophore and the racemic 2-methyl-1-butanol. It should contain both the spectral signature of the *R*−*R* and *R*−*S* complexes. In fact it is exactly composed of the superposition of the spectra in Figures 3a,c. This result shows that the *S*−*S* and *R*−*R* complexes display the same spectroscopic fingerprint and cannot be distinguish as it is expected from the enantiomeric mirror image property of these two forms. It should be added that the excitation spectrum of the mixture of both complexation partners in their racemic forms is exactly identical to that of Figure 3b.

Fluorescence decay times have also been determined for the selective excitation of several bands of the *S*−*S* and *R*−*S* complexes (Table 1). In both cases the lifetime is much longer than that of the bare molecule (45 ns for the vibrationless level). As mentioned before, a similar effect has been observed for complexes with nonchiral alcohols and is not related to the chirality of the systems but to the photophysics of the naphthalene chromophore. It should be mentioned, however, that, because of this peculiar sensitivity of the excited state dynamics to the subtle perturbation induced by complexation, the decay time can also be used to probe chirality dependent properties.

(D) Complexes of 2-Naphthyl-1-ethanol with Secondary Chiral Alcohols. The fluorescence excitation spectrum of (*S*)- and (*R*)-2-NetOH in the presence of 2-butanol, 2-pentanol, 2-hexanol and 2-octanol are presented on Figures 4 and 5. The spectrum obtained when the complexing solvent is in its racemic form are shown in Figure 4, while in Figure 5a, b the spectra obtained with pure enantiomeric forms in the case of 2-pentanol are shown as an example. The spectra obtained for the homochiral and heterochiral mixture are different and allow an assignement of the features belonging to the *S*−*S* (*R*−*R*) and *S*−*R* (*S*−*R*) diastereoisomers in the racemic mixture. Similar experiments have been performed for the enantiomers of the other secondary alcohols in order to identify the bands corresponding to the homochiral or heterochiral pairs (Table 2). The spectra appear to be complex and do not display a regular pattern from which some propensity rules can be easily deduced. However, in each case, the most red feature originates from the heterochiral complex and is systematically followed by low-frequency bands. This behavior is particularly clear in the case of 2-pentanol and 2-octanol and can be related to the effect of increased alkyl chain length of the complexing alcohol which may induce an activity in intermolecular low frequency modes.[16] On the other hand, the first band of the homochiral complex is

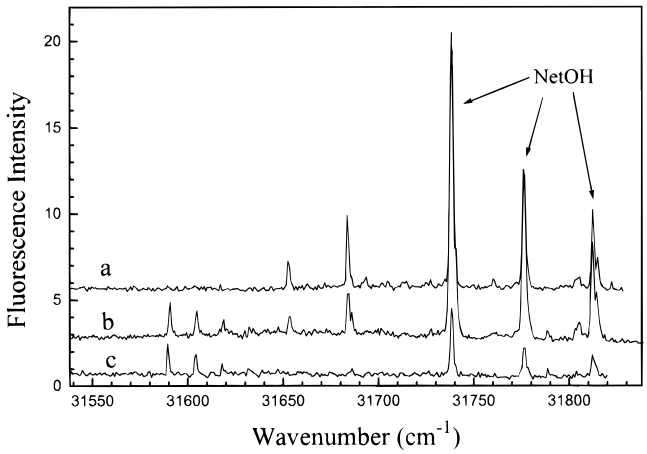

Figure 5. Fluorescence excitation spectra showing chiral discrimination in the complexes of 2-NetOH with 2-pentanol used (a) in their *R*−*R* enantiomeric forms, (b) in the racemic mixture, and (c) in their *R*−*S* enantiomeric forms, respectively.

TABLE 2: Shifts of the Main Bands of Complexes of 2-NetOH with Secondary Alcohols

complexing alcohol	complex *R*−*S* (*S*−*R*)	complex *R*−*R* (*S*−*S*)
2-butanol	−136	−125
	−114	−87
	−73	−69
	−28	+29
	+6	
2-pentanol	−147	−85
	−133	−54
	−119	
	−52	
	+50	
2-hexanol	−127	−106
	−110	−73
	+53	−65
2-octanol	−160	−133
	−151	−122
	−142	−115
	−135	−107
	−17	−91
		−79
		−63
		−38

relatively weak with respect to the most intense one which appears further to the blue and this may indicate the presence of different conformations of the complex as suggested previously for the primary alcohols.

Concluding Remarks

The present study has proved that enantioselective complexation in isolated van der Waals complexes demonstrates chiral recognition at the molecular level through the use of laser induced fluorescence spectroscopy. The separation observed here confirms that diastereoisomers are stabilized in the supersonic expansion into two noninterconverting minimum energy geometries differing by their energy of formation. Besides its resolving capability (separation of diasteroisomers electronic transitions with a resolution of 1 cm^{-1} can be routinely achieved in the laser-induced excitation spectra) and analytical interest, this method may provide valuable informations on two points.

The first point of concern is related to the understanding of the nature of stereochemically dependent interactions that control this enantioselectivity. Although this analysis cannot be made without the help of calculations of the most stable geometries, one may attempt to draw from the experimental results some qualitative guiding trends. It is interesting in this respect to refer to the mechanistic concepts advanced by Pirkle[1] concerning the chromatographic separation of enantiomers on chiral stationary phases. According to Pirkle, chiral recognition requires a minimum of three simultaneous interactions with at least one of these interactions involving stereochemically dependent factors. As stated before, in the systems under study containing a OH functional group in each species, the OH···O hydrogen bond is expected to provide one of these point interactions with the naphthyl ethanol acting as the hydrogen bond donor. Other localized interactions are not quite so simple to visualize for molecular pairs consisting of complex polyatomic alcohols with different side chains which may take several conformations. However, the OH···O bond strength is not expected to be significantly different for the *R*−*S* and *S*−*S* complexes of a given alcoholic solvent and is probably not the discriminating factor. The mutual orientation and steric repulsion of the alkyl substituents of the solvent with respect to the naphthalene ring of the chromophore are presumably playing the determining role for the spatial enantiodifferentiation. Preliminary calculations, based on the exchange perturbation method,[17] indicate that the arrangement of substituents around the intermolecular hydrogen bond may take either an extended configuration minimizing the steric hindrance, or a folded one involving additive dispersive interactions of the alkyl groups with the naphthalene ring. Dispersive interactions are expected to be more sensitive to the spatial orientation of the substituent and thus to the chirality. It is interesting in this respect to compare the spectral properties of the complexes of 2-NetOH with primary linear alcohols and secondary chiral alcohols and to stress the similarity between the excitation spectra obtained with 1-propanol (Figure 1c) and 2-butanol (Figure 4d) or and to a less extend between 1-butanol (Figure 1d) and 2-pentanol (Figure 4c), respectively. The secondary alcohols differ from the primary ones by the introduction of a methyl group in the 1-position. For 1-propanol and 2-butanol, the spectra exhibit the same series of weak bands toward the red followed by a stronger doublet further to the blue. In the case of complexes with 2-butanol, these features belong clearly to different diastereoisomers and one may postulate a direct correspondence between the structures of the complexes with primary alcohols and the diastereoisomers evidenced with secondary alcohols. As suggested before in the case of 1-propanol, the peculiar pattern of the excitation spectrum seems to be related to the presence of different structural isomers. Under this latter assumption, one can consider that the stronger dispersive interactions due to a folded geometry would enhance the red shift of the probed $\Pi-\Pi^*$ electronic transition of the naphthalene chromophore and induce low frequency intermolecular vibrations as it has been shown in the complexes of perylene with alkanes.[16] One thus may speculate that such a structure is responsible for the weak red band systems. Conversely, in an extended (or less folded) configuration, one may expect a reduced red shift and no activity in the intermolecular vibrations together with no effect with increasing chain length. The most intense transition present in all complexes may then be assigned to an extended configuration. As mentioned above, the similar behavior observed in the case of the complexes with secondary alcohols may indicate that the homochiral complex adopts an extended geometry while the heterochiral pair for these systems should take a folded configuration with the longest alkyl substituent interacting with the aromatic nucleus of the chromophore.

The second interesting aspect of this method deals with the relationship between the microscopic solvent shifts and the absolute conformations. Complexation of 2-NetOH with chiral

alcohols as well as with nonchiral alcohols induces a small red shift of the bare chromophore S_0-S_1 transition. This result indicates that the interaction potential minima are slightly deeper (by $\sim$100 cm^{-1}) in the excited state with respect to the ground state and thus that the binding energy between the two components of the complexes is increased by about 10% after electronic excitation. This added stabilization is commonly observed in van der Waals complexes and reflects the increased polarizability of the excited state. However, the small spectral splitting between the diastereoisomers, which represents the relative energy gap between the differential bonding energies in the excited state and in the ground state of *S*−*S* versus *R*−*S* pairs, cannot be used to determine whether the homochiral or heterochiral pair is more stabilized in the ground state. One should emphasize in this respect the different behavior of primary alcohols versus secondary alcohols as chiral complexing agents when comparing for example the spectral shifts of the diastereoisomers formed with 2-methyl-1-butanol (Figure 3) and 2-pentanol (Figure 5). Both solvents differ only by the position of the asymetric carbon which is in the 2-position in the former case and in the 1-position in the latter one. The relative energy difference between the homochiral *S*−*S* (respectively *R*−*R*) and heterochiral *R*−*S* (respectively *S*−*R*) transition energies is 49 cm^{-1} (140 cal mol^{-1}) for 2-methyl-1-butanol. For chiral secondary alcohols the transition energy order is reversed. The heterochiral association leads to the larger red shift and the energy difference between the first feature of the heterochiral complex and the most intense band which belongs to the homochiral complex is on the order of 70 cm^{-1} (200 cal mol^{-1}). This difference cannot be understood in a simple way at the present stage and raises the question of the relative stability of enantiomeric pairs in the ground and excited states. It may be assumed that the most red-shifted transition corresponds to the pair with the largest bonding energy in the ground state, indicating that the relative stabilization energy difference between the two pairs is further enhanced in the excited state as can be predicted if the dispersive forces play a determinant role in the discrimination process. This would imply that the *R*−*R* (*S*−*S*) interaction is higher for the primary alcohol than the *R*−*S* (*S*−*R*) interaction while the reverse situation holds for the complexes with secondary alcohols. Under this assumption, the present results show that the relative stability of diastereoisomeric pairs is extremely sensitive to minute stereochemical effects such as those resulting from the position of the chiral center. Otherwise, one may consider that the same chiral pair is the most stable for both cases . The reverse order of the *R*−*R* versus *R*−*S* shifts in the complexes with primary and secondary alcohols would reflect thus a more subtle influence of the electronic excitation of the chromophore on the relative stability of the enantiomeric pairs.

Semiempirical calculations based on perturbation exchange theory[17] are in progress to try to distinguish between this alternative and will be reported in the near future.

References and Notes

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