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Laser induced fluorescence of jet-cooled complexes between chiral molecules: a photophysical method for chiral discrimination

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Abstract

Laser induced fluorescence of jet-cooled van der Waals complexes of chiral molecules has been used to study the chirality-dependent excited state dynamics in an isolated molecular pair. The complexes under study comprise a chiral chromophore (α-methyl-2-naphthalene-methanol) complexed by a chiral solvent (a secondary chiral alcohol or camphor).

For chiral secondary alcohols, the excitation spectrum of the heterochiral and homochiral complexes differ from one other: this shows unambiguously that diastereoisomeric weakly bound complexes with different binding energies both in the ground state and in the excited state can be isolated under supersonic jet conditions. The difference in their fluorescence lifetimes has been related to a difference in the energy gap between the optically excited state and a close-lying triplet state, which leads to an enantioselectivity in the intersystem crossing efficiency.

The homochiral and heterochiral complexes of camphor display the same excitation spectrum. Although no enantiodifferentiation can be achieved on the basis of the transition energies, a dramatic difference has been observed in the fluorescence lifetime of the diastereoisomers. This difference has been tentatively explained in terms of a chirality-dependent energy transfer between the optically excited chromophore and the close-lying n–π^* state of camphor.

These results show that the fluorescence lifetime of a chromophore can be used as a very sensitive probe for studying the chirality dependence of electronic coupling within a van der Waals complex under supersonic jet conditions. © 1997 Elsevier Science S.A.

Keywords: Chirality; Laser induced fluorescence; Supersonic jet; van der Waals complex

1. Introduction

The dependence of numerous biochemical processes, such as enzymatic catalysis or activity of drugs, upon the chirality of the reactants is of the widest importance in life chemistry [1]. Intermolecular chiral recognition is also at the basis of chemical methods which allow discrimination between enantiomers and separation of them [2–4]. The observed enantiodifferentiation is related to the formation of diastereoisomers, eventually through the existence of transient complexes, that must differ in their free energy of formation: two enantiomers can be chromatographically separated on a chiral stationary phase if diastereoisomeric adsorbates are formed from the chiral phase and the enantiomers and if they differ in their free energy of formation. Empirical models such as the "three point interaction" rule accounting for the chromatographic separation of enantiomers have been proposed, and have demonstrated the importance of short range interactions in chiral discrimination [3]. We have recently undertaken a spectroscopic study of the enantioselectivity which may arise from the formation of van der Waals complexes in the gas phase [9]. The aim of this work is to obtain information from a molecular viewpoint about the specificity of the interactions and the structure of the weakly bound species involved in chiral recognition. Moreover, the formation of weakly bound diastereoisomeric complexes in a supersonic expansion can be used as an analytical tool to discriminate between enantiomers. Chirality-dependent molecular interaction may also exist in the excited state and is responsible for the enantioselectivity observed in photophysical or photochemical processes in asymmetric systems [2,5]. A chirality dependence of electron transfer and fluorescence quenching dynamics has been observed in solution [5,6] in the case of 1,1′-binaphthyl and (*R*)- and (*S*)-*N*,*N*′-dimethyl-1-phenyl-2-ethylamine. A marked enhancement of the optical activity associated with enantioselective excimer formation [7] has also been observed in the case of pyrene substituted with a chiral group in the 1-position. Of particular interest

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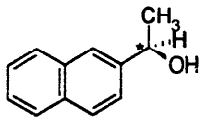
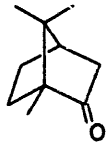


α-methyl-2-naphtalene-methanol



camphor

Scheme 1.

are the time-resolved chiroptical luminescence measurements [8] used to study chirality-dependent energy transfer in solutions [8b]. In all the cases mentioned above, the enantioselectivity achieved in the mechanism proceeds through a transient encounter complex, the relative stability and structure of which govern the selectivity of the process. However, the enantioselectivity of these photochemical or photophysical processes is usually low and is often limited by an epimerization process faster than the reaction itself. By freezing the diastereoisomeric weakly bound complexes, one can study the chirality dependence of the elementary photophysical processes in an isolated molecular pair without any influence from collisions or the bulk material. When the complexes under study comprise a fluorescent chiral chromophore complexed by a chiral solvent, lifetime measurements may be used as a diagnostic tool for the dependence of the excited state dynamics of the chromophore upon the chirality of the solvent. We have chosen a naphthalene derivative as chromophore because the excited state lifetimes of naphthalene derivatives are known to be strongly dependent on the substituent position [10,11], excess energy [10,12], and complexation [9,10,12]. Fluorescence lifetimes can thus be used as a very sensitive probe for the stereochemical factors that govern the interaction and geometry of a complex formed between chiral molecules.

The system under study consists of a chiral 2-substituted naphthalene as the chromophore [(*R*)-(+)- or (*S*)-(−)-α-methyl-2-naphthalenemethanol, hereafter denoted by NaphMeOH] and a chiral secondary alcohol or bicyclic molecule as the complexing agent. In both cases, the chirality of the molecule is due to the presence of an asymmetric carbon (see Scheme 1). The interacting molecules in the two (*R*:*R*) and (*R*:*S*) van der Waals complexes are expected to behave in a different way and we expect a different spectroscopic fingerprint according to whether the (*R*:*R*) or the (*R*:*S*) pair is excited. We will focus in this paper on the chirality dependence of the excited state lifetimes. The structural aspects will be discussed in a forthcoming paper [13].

2. Experimental

The principle of the experiment rests on the laser excitation of the van der Waals complexes formed in a continuous supersonic expansion of helium (2–3 atm). The carrier gas is seeded by mixing a helium flow saturated with the solvent with a second flow passing over a (*R* or *S*) NaphMeOH sample located just before the expansion jet. The sample is heated to about 70°C in order to increase its vapour pressure. Camphor is heated slightly to increase the intensity of the feature due to the complex. The alcohols used as complexing agents are used at room temperature. The molecules and van der Waals complexes are excited in the cold region of the jet by means of a frequency-doubled dye (Rh640 and DCM) laser pumped by the second harmonic of a YAG laser (Quantel). The fluorescence is observed directly through a Schott WG 335 filter by a Hamamatsu R2059 photomultiplier. The signal is monitored by a Camac ADC (Lecroy 2249 W) connected to a PC microcomputer. The lifetimes are recorded by means of a digital oscilloscope (Lecroy 9401) operating in the sweeping mode. The temporal resolution is about 8 ns. The complexing agent and the chromophore, in either the racemic or the resolved forms (enantiomeric purity 99%), are purchased from Aldrich and used without further purification.

3. Results and discussion

3.1. Bare molecule

The spectroscopy of NaphMeOH has been reported previously [9]. The laser induced fluorescence (LIF) excitation spectra of the racemic NaphMeOH and of both (*R*)- and (*S*)-NaphMeOH are strictly identical, as expected for linear polarization of the laser. The spectrum exhibits three main bands at the origin (Fig. 1). The 0–0 band is located at 31 741 cm^{-1} and followed by two intense features located at 39 and 76 cm^{-1} respectively, which appear in combination with the main vibration bands. The emission spectra resulting from the excitation of the 0° or the 0° + 39 cm^{-1} level show a low frequency mode (45 cm^{-1}) which is the counterpart of the

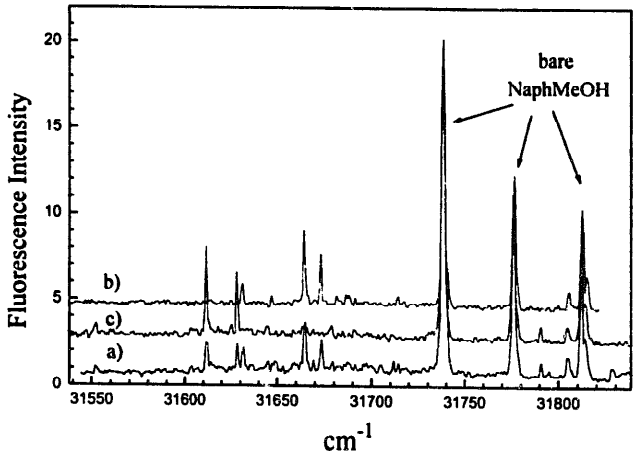


Fig. 1. Fluorescence excitation pectrum of the NaphMeOH:2-hexanol complex: (a) racemic samples; (b) (*S*)-2-hexanol:(*S*)-NaphMeOH; (c) (*R*)-2-hexanol:(*S*)-NaphMeOH.

39 cm^{-1} mode observed in the excitation spectrum. This mode has been assigned to a torsion of the side chain.

The fluorescence lifetimes decrease from 45 ns for the 0° level to 35 and 20 ns for the levels located at 39 and 76 cm^{-1} respectively.

3.2. Complexation with 2-hexanol: lengthening of the lifetime

When the racemic chromophore is complexed with 2-hexanol, two series of bands are observed (Fig. 1(a)), which have been assigned to the homochiral (*S*:*S*) (Fig. 1(b)) or the heterochiral (*R*:*S*) (Fig. 1(c)) complex respectively. This assignment rests on a comparison with the fluorescence excitation spectra of optically pure mixtures (Fig. 1(b) and 1(c)). These results show unambigously that an enantiodifferentiation is achieved in the van der Waals complex formation in the ground state. The (*R*:*R*) [or the (*R*:*S*)] complex displays exactly the same spectroscopic properties as the (*S*:*S*) [or the (*S*:*R*)] complex, according to mirror symmetry considerations.

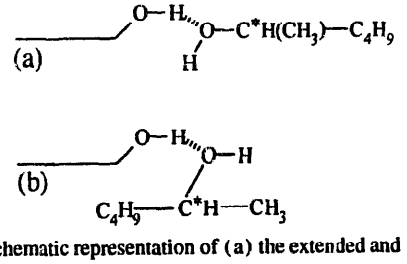
The heterochiral (*R*:*S*) complex exhibits a larger red-shift of the electronic transition than the homochiral (*R*:*R*) complex (127 cm^{-1} vs. 73 cm^{-1} for the origin of (*R*:*S*) and (*R*:*R*) respectively). A larger red-shift of the transition for the heterochiral complex seems to be a general trend for complexes of NaphMeOH with linear secondary alcohols [13], and can be used as a tool for the determination of the absolute conformation of an alcohol of this series. The difference between the (*R*:*R*) and the (*R*:*S*) transition energies is around 50 cm^{-1} ($\approx$0.15 kcal mol^{-1}), that is, 5–10% of the binding energy of the complex, which has been estimated to be around 2–4 kcal mol^{-1}. This estimate has been deduced from a comparison with the binding energy of the model complex with methanol [13], which was measured as being between 600 and 900 cm^{-1} ($\approx$2 kcal mol^{-1}).

The fluorescence excitation spectrum of the complexes shows a vibrational pattern which differs from that of the bare molecule. The 39 cm^{-1} mode, which has been assigned to a torsional motion located on the side chain, is not observed in the complex. This can be taken as an indication of an interaction between the chromophore and the solvating agent located on the side chain of the chromophore, which leads to a strong hindrance to rotation. The origin is followed by a second intense band located at 8 cm^{-1} for the (*R*:*R*) and 17 cm^{-1} for the (*R*:*S*) complex respectively. These bands can be due either to a very low frequency intermolecular motion (wagging motion of the alcohol relative to the naphthalene frame) or to the existence of two conformational isomers: hole burning experiments are planned to resolve this question.

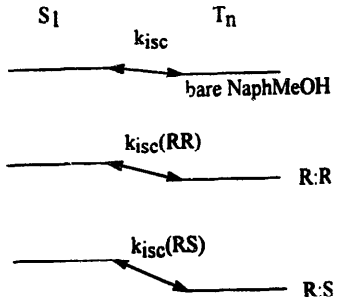
Preliminary calculations based on the exchange-perturbation method [14] have been performed on similar systems (complexes of NaphMeOH with non-chiral alcohols such as propanol or chiral alcohols such as 2-chloro-1-propanol) and have indicated that the complexation site is actually the side chain of the chromophore and that NaphMeOH acts as an hydrogen donor towards the solvent: the electrostatic contribution (due mainly to the hydrogen bond) is about 50% of the attractive part of the interaction energy. Several isomers of the complexes have been calculated, which are related either to the internal conformation of the alkyl chain of the solvent or to the intermolecular geometry. These isomers can be divided into two classes, both of which involve the strong H-bond as the main interaction; see Scheme 2. The first one is an "extended" geometry, in which the alkyl chain of the solvent lies far away from the naphthalene aromatic ring. In addition to the main electrostatic H-bond interaction, a small additive electrostatic interaction is favoured in this conformation relative to the repulsion–dispersion part of the interaction energy. The second class is a "folded" conformation in which the alkyl chain of the solvent, which bears the asymmetric carbon and thus the chiral part of the molecule, is folded on the aromatic framework, which leads to an additive dispersive interaction. In this type of conformation the dispersion–repulsion part of the interaction energy is optimized relative to the electrostatic part. It can be noted that this folded conformation is much more sensitive to steric factors than the extended one: the potential energy surface is expected to be less shallow because of the interaction between the π electron of the naphthalene frame and the alkyl chain of the solvent. For example, the interaction energy of the folded conformation of the (NaphMeOH:2-chloro-1-propanol) complex has been calculated to be much more chirality-dependent than that of the extended conformation [15].

We have assumed that the same hypothesis may hold for the (NaphMeOH:2-hexanol) complex. As the total interaction energy and thus the equilibrium geometry is a subtle balance between the electrostatic and repulsion–dispersion components of the interaction energy, which in turn are sensitive to the stereochemical factors, the conformation adopted by the complex (either folded or extended) will be very sensitive to the balance between the forces at play. As the interaction energy of the extended conformation is not chirality-dependent, a chiral discrimination in the transition energy will be achieved if at least one of the (*R*:*R*) or the (*R*:*S*) complex can adopt a folded geometry. Detailed calculations are in progress to confirm these hypotheses and to aid in the determination of the geometry of the complex [15].

The lifetime of the 0° level of the (*R*:*R*) complex is shorter than that of the (*R*:*S*) complex, and both are longer than that of the bare molecule (55 ns, 140 ns, and 45 ns respectively). Whereas the bare molecule and the heterochiral complex



Scheme 2. Schematic representation of (a) the extended and (b) the folded geometry of the NaphMeOH:2-hexanol complex.



Scheme 3. Schematic diagram of the energy levels involved in intersystem crossing in the bare molecule and in the homo- and the heterochiral complexes.

show a slight decrease of the fluorescence lifetime when the excess energy is increased, the opposite behaviour is observed for the homochiral complex: the band located at $+8\ cm^{-1}$ from the origin of the complex displays a longer lifetime (75 ns, vs. 55 ns for the origin). A lengthening of the fluorescence lifetime relative to the bare molecule has been observed for other complexes of NaphMeOH [9,15], but the lifetime is not always chirality-dependent [9]. A shorter lifetime for the 0° level and a lengthening of the lifetime upon complexation have already been observed in other naphthalene derivatives [10,12]. We reported, for example, that the 0° level of 1-cyanonaphthalene exhibits a shorter lifetime relative to higher vibronic levels and that its lifetime is increased by complexation with acetonitrile. Comparison between the fluorescence excitation and phoshorescence excitation spectra has shown that this unusual behaviour is due to an increase in the intersystem crossing efficiency for the 0° level, probably because of an accidental coincidence between the optically excited state and a close-lying triplet state [12]. A similar explanation may be invoked in the case of the NaphMeOH:2-hexanol complexes: complexation leads to a detuning between the optically excited S_1 state and the promotional T_n level and thus to a decrease in the intersystem crossing (ISC) efficiency and a lengthening of the fluorescence lifetime. The intersystem crossing rate constant is different for the homochiral and the heterochiral pairs because of a modification of the triplet vs. the singlet interaction energy (see Scheme 3).

The decrease of the ISC efficiency may also be due to a modification upon complexation of low frequency modes, which are known to play an important role in promoting ISC [16]. As mentioned earlier, the rotation of the side chain is strongly hindered in the complex and could be a good candidate for that role. In this case, the modification of the 39 cm^{-1} mode would be different in the homochiral and the heterochiral pairs.

3.3. Complexation with camphor: shortening of the lifetime

The fluorescence excitation spectrum of the (±)-NaphMeOH:camphor complex displays an intense single band red-shifted by 89 cm^{-1} from the origin of the bare molecule. The same spectrum recorded with pure enantiomers (see Fig. 2(a) and 2(b)) has shown that both diastereoisomers absorb at exactly the same wavelength, at least with the available resolution (laser bandwidth of 0.5 cm^{-1}). Note that the relative intensity of the bands observed in the fluorescence excitation spectrum of the (*R*:*R*) and the (*R*:*S*) complex respectively does not reflect the ratio between the lifetimes: the homochiral complex displays a longer lifetime but a weaker fluorescence intensity than the heterochiral complex. This arises from the well known property of an eutectic mixture: when (*S*)-camphor is mixed with racemic NaphMeOH, the (*S*)-enantiomer of NaphMeOH is more easily evaporated than the (*R*) one. The relative intensities must thus be considered carefully and no conclusion can be drawn. The intensity dependence upon camphor concentration of the band assigned to the complex was not clear, and a REMPI spectrum has been recorded. As the ionization potential of the bare molecule is more than twice the S_0–S_1 transition energy, we have used a two colour, two photon ionization process and have checked that this band was due to a 1:1 complex. The spectrum is presented in Fig. 2(c) and displays the same band as that observed in the LIF spectrum, located at $-89\ cm^{-1}$ from the bare molecule origin. This band is followed by bands of very low intensity located at 15 and 25 cm^{-1} from the origin and a strong band located at 165 cm^{-1} from the origin. This band has not been observed in the fluorescence excitation spectrum because it is hidden by the much more intense band of the bare molecule ($0_0^0+76\ cm^{-1}$) which is located exactly at the same energy. The fluorescence intensity observed with excitation at this wavelength does not depend on camphor concentration: the fluorescence yield of the NaphMeOH:camphor complex excited at this energy must be very low. As this level is not seen in fluorescence, but can be observed in a two photon, two colour ionization process, one can estimate its lifetime as being in the range 100 ps–1 ns. No discrimination can be achieved between the (*R*:*R*) and the (*R*:*S*) complex on the basis of the excitation energy. A possible explanation may be provided by the peculiar shape of the camphor molecule, which is very rigid. The

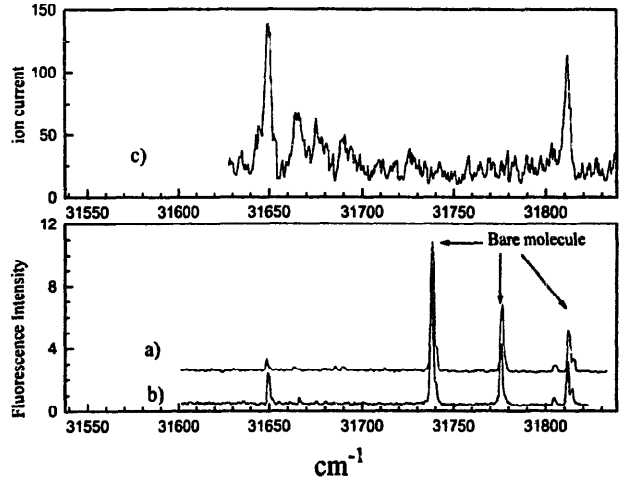


Fig. 2. (a) Fluorescence excitation spectrum of the NaphMeOH:camphor (*R*:*R*) complex; (b) fluorescence excitation spectrum of the NaphMeOH:camphor (*R*:*S*) complex; (c) REMPI spectrum of the NaphMeOH:camphor complex.

Table 1
Lifetime of the 0° level of the heterochiral (*R*:*S*) and homochiral (*R*:*R*) complexes of NaphMeOH. Note that, for the NaphMeOH:camphor complex, there is an additive intense band located at +76 cm^{-1} from the bare molecule origin and not detectable in fluorescence

Complex	Shift from the bare molecule origin/cm^{-1}	Lifetime/ ns
2-hexanol (*R*:*R*)	−73	(55±3)
	−65	(75±4)
2-hexanol (*R*:*S*)	−127	(140±5)
	−110	(120±5)
camphor (*R*:*R*)	−89	(25±3)
camphor (*R*:*S*)	−89	(42±3)
bare molecule	0	(45±3)
	+39	(35±3)
	+76	(20±3)

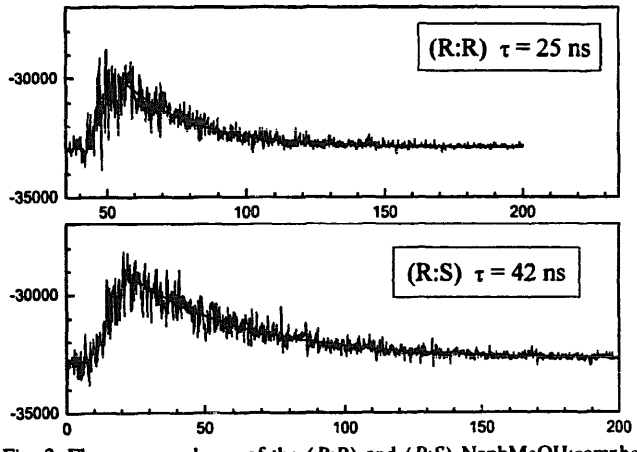


Fig. 3. Fluorescence decay of the (*R*:*R*) and (*R*:*S*) NaphMeOH:camphor complexes.

main interaction between NaphMeOH and camphor is expected to take place between the hydroxy group of NaphMeOH and the keto group of camphor: there is thus no possibility for the camphor molecule to attain the folded geometry which has been supposed to be responsible for chiral discrimination. This contrasts with the floppy 2-hexanol molecule previously described.

In contrast with the excitation spectra, the lifetimes of the (*R*:*R*) and (*R*:*S*) complexes differ markedly one from the other (see Table 1 and Fig. 3). Both of them are shorter than that of the bare molecule, slightly for the heterochiral complex (42 ns) and strongly for the homochiral complex (25 ns).

This difference is really dramatic: let us note that the excitation wavelength is exactly the same for the (*R*:*R*) and (*R*:*S*) pairs. To explain this surprising behaviour, we can not totally rule out the hypothesis of a very efficient intersystem crossing in the NaphMeOH molecule itself. However, this assumption does not seem plausible because all the complexes of NaphMeOH with various classes of molecules [13,14] show a longer lifetime than the bare molecule except that with camphor. A more plausible explanation for this is a reversible energy transfer between the optically excited state and a close-lying n–π^* state of camphor. Because the n–π^* transition of camphor is very weakly allowed, a Förster mechanism involving coupling between the transition moments is not expected, and a Dexter mechanism involving a short range transfer by means of forbidden transitions [17] must be responsible for the transfer. The factor of importance for this mechanism is the overlap between the excited state orbital of the donor and that of the acceptor. If the process responsible for the shortening of the lifetime is the energy transfer, this means that the electronic overlap between the donor and the acceptor within the complex is more chirality-dependent than the interaction energy. It should be noted that the donor and acceptor transition energies must be very close to one other, which leads to a reversible transfer: for an excess energy of 165 cm^{-1}, the transfer becomes non-reversible and the transition of the complex is not observed in the fluorescence excitation spectrum because of a very low fluorescence quantum yield.

4. Conclusions

These results show that the fluorescence lifetime of a chiral chromophore complexed by a chiral solvent under supersonic jet conditions is a very sensitive probe for chirality-dependent excited state dynamics. For 2-hexanol, the excitation spectrum of the heterochiral and homochiral complexes differ from each other and the difference in their fluorescence lifetimes has been related to an enantioselectivity in the intersystem crossing efficiency.

For the NaphMeOH:camphor complex, both diastereoisomers absorb at exactly the same wavelength and no discrimination between the (*R*:*R*) and (*R*:*S*) pairs can be made on the basis of the excitation energy. However, their lifetimes differ strongly, which has been tentatively explained in terms of a chirality-dependent energy transfer between the optically excited chromophore and the close-lying n–π^* state of camphor.

It should be stressed that the factor of 2 between the fluorescence lifetime of the (*R*:*S*) and the (*R*:*R*) complex excited at exactly the same energy is very high when compared with the effects of 1–5% observed for the enantioselectivity of fluorescence quenching in solution [5,6].

Experiments with other chiral chromophores, such as the benzene analogous of NaphMeOH, are in progress to provide evidence of photoinduced chirality-dependent reactions.

Acknowledgements

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