

## Isomerism in jet-cooled 1-cyanonaphthalene complexes

F LAHMANI\*, A ZEHACKER-RENTIEN and E BREHERET

Laboratoire de Photophysique Moléculaire, Bât. 213–Université de Paris-Sud, 91405–Orsay Cedex, France

**Abstract.** The effect of complexation on the first electronic transition of 1-cyanonaphthalene has been studied for complexes with aprotic polar solvents (acetonitrile, diethylether) or olefins (2-methyl-2-butene, 2,3-dimethyl-2-butene). In both cases, isomerism has been evidenced.

With polar solvents, two strong absorption bands appear in the  $0_0^0$  region, one being shifted to the red and the other one to the blue side of the bare cyanonaphthalene transition. These two bands have been assigned to two isomeric forms involving specific interactions between the solvent and the cyanonaphthalene molecule. These isomers have been shown to interconvert at higher vibronic energies.

With the 2,3-dimethyl-2-butene a broad absorption band leading to a red shifted fluorescence has been observed and assigned to an exciplex. With the 2-methyl-2-butene, one observes the superposition of narrow and broad bands in the excitation spectrum. These two systems have been assigned to two isomeric forms, one of them crossing to an exciplex in the excited state. At higher vibronic energy, emission from the two conformers is observed.

**Keywords.** Supersonic jet; van der Waals complexes; exciplex; isomerisation; naphthonitrile; laser spectroscopy.

### 1. Introduction

The generation of molecular complexes of weak binding energy in a supersonic expansion provides an unique way to study in isolated conditions the interaction between molecules (Levy 1980, 1986). When combined with laser excitation, this method allows the investigation, at the molecular levels, of the modification of excited states properties (energy levels, relaxation processes) induced by the presence of a perturbing ligand.

Among the bimolecular processes related to the photochemistry in solution the solvation effects (Gibson *et al* 1988) and the exciplex formation (Castella *et al* 1989) in systems involving strong electrostatic interactions are of great interest. Both processes may depend strongly on the geometry of the molecular complex cooled in the supersonic jet (Motyka *et al* 1989; Piuzzi and Tramer 1990). Furthermore molecular rearrangement in the excited state of the bimolecular complexes may also induce the formation of low energy excited states which cannot be reached by direct Franck–Condon excitation.

In this paper, we report experimental evidence of the formation of different isomers both in the ground and excited states of 1:1 complexes of 1-cyanonaphthalene with either polar solvent molecules or electron donors such as methylated ethylenes.

---

\* For correspondence

## 2. Experimental

The supersonic jet is obtained by expanding the gaseous mixture (1–2 atm helium total pressure) through a 200  $\mu\text{m}$  nozzle. The molecules are excited by a dye laser (DCM) pumped by a B M Industrie YAG laser and frequency doubled by an angle tuned KDP crystal. The emitted fluorescence is collected through a filter (WG 345 or 6-G 375), or through a Jobin Yvon 60 cm monochromator or directly focused on the slit of a photomultiplier (XP 2020) and monitored with a homemade CAMAC interface and a PC XT computer.

### 2.1 Complexes of 1-cyanonaphthalene with polar solvents

The fluorescence excitation spectra of 1-cyanonaphthalene (1-CNN) complexed with aprotic solvents such as acetonitrile (AN) or diethylether (DEE) show the appearance of two series of new features (figure 1). One system is shifted towards the red side of the free molecule main transitions while the second system is blue-shifted. The red shift is about  $-175\text{ cm}^{-1}$  and  $-117\text{ cm}^{-1}$  and the blue shift is  $+40$  and  $+28\text{ cm}^{-1}$  respectively for the 1-CNN:AN and the 1-CNN:DEE complexes. A solvatochromatic red shift is usually observed in the complexes of aromatic molecules and indicates a stabilisation of the excited complex with respect to the ground state. The ratio of the intensities of the blue and red features does not depend on the partial pressure of the solvent molecule between 0.5 and 5 torr indicating that these bands correspond to 1:1 complexes.

The dispersed fluorescence spectra following excitation of the red and blue features (noted  $R_0$  and  $B_0$ ) at origin have their origins centered at the excitation wavelength and show roughly the same vibrational pattern as the fluorescence from the  $0^0$  level of the free 1-CNN, although some differences can be seen in the Franck–Condon envelop and ground state frequencies. Similarly slight changes of the excited state frequencies and intensity distribution of the vibronic transitions of the 1-CNN molecule are observed in the fluorescence excitation spectra. Moreover the fluorescence lifetimes of the complexes excited at both the blue ( $= 37\text{ ns}$  for 1-CNN:AN and  $33\text{ ns}$  for 1-CNN:DEE) and the red ( $= 52\text{ ns}$  for both complexes) origins are different from each other and are lengthened with respect to the fluorescence lifetime from the free molecule  $0^0$  level ( $= 22\text{ ns}$ ). All these data may be interpreted by the presence of two isomers involving different orientations of the solute and solvent molecules.

This assumption is corroborated by the study of fluorescence spectra and lifetimes obtained by the excitation of higher internal vibronic states of the 1-CNN complexes. Figure 2 shows the emission spectra resulting from the excitation of the bands noted  $B_1$ ,  $B_2$ ,  $B_3$  correlating respectively with the vibronic levels of 1-CNN at 404, 451,  $510\text{ cm}^{-1}$  from the origin and  $R_2$ ,  $R_3$  and  $R_4$  at 451, 510 and  $663\text{ cm}^{-1}$ . From these spectra, it can be seen that whereas the excitation of the  $R_2$  and  $R_3$  or  $B_1$  and  $B_2$  features leads to a main emission band at the  $R_0$  or  $B_0$  energy, excitation of  $R_4$  or  $B_3$  gives rise to both  $R_0$  and  $B_0$  emission. This result gives clear evidence that the two absorption systems correspond to two different isomers of the 1-CNN:AN complexes which interconvert in the excited state. The barrier to isomerisation is located between  $510$  and  $663\text{ cm}^{-1}$  above the origin of the red shifted isomer which is the more stable form in the excited state. The blue shifted form is estimated to be the most stable in the ground state. A similar behaviour is observed in the case of

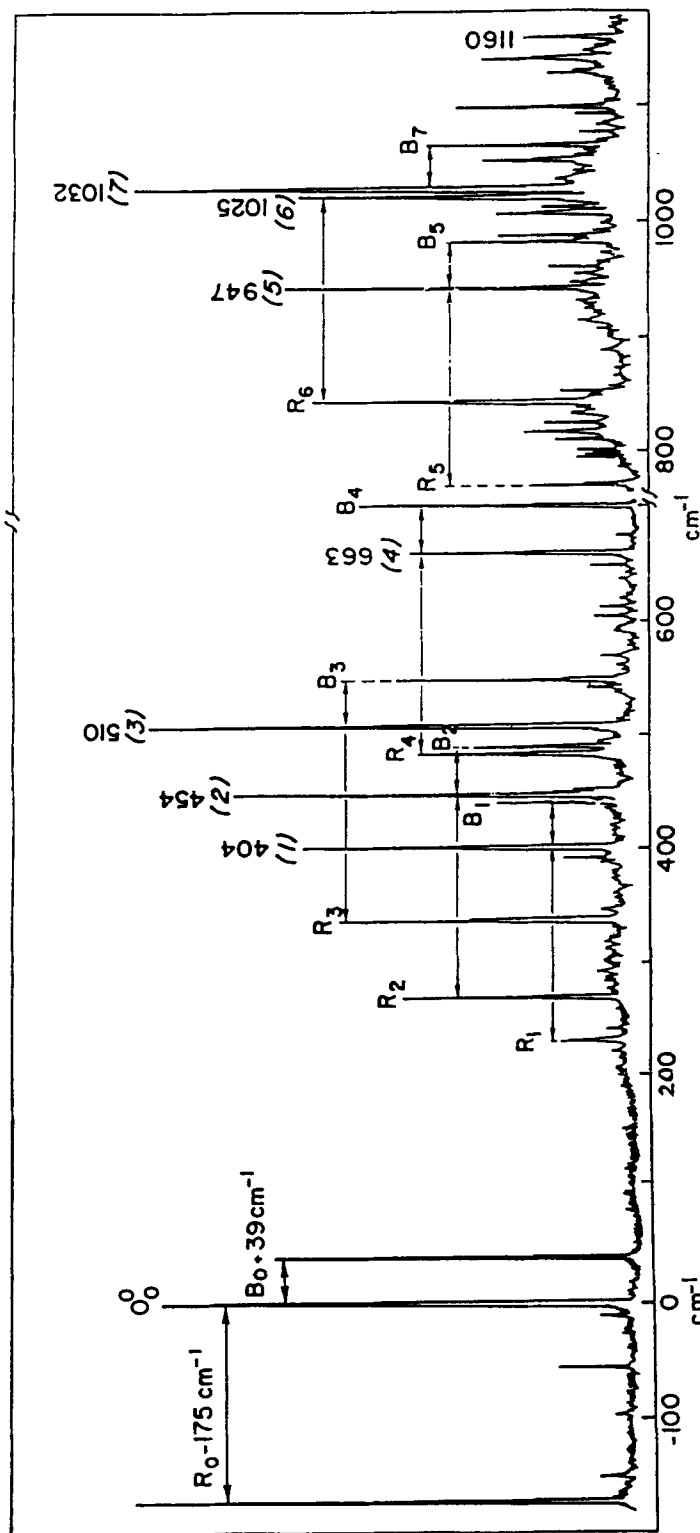
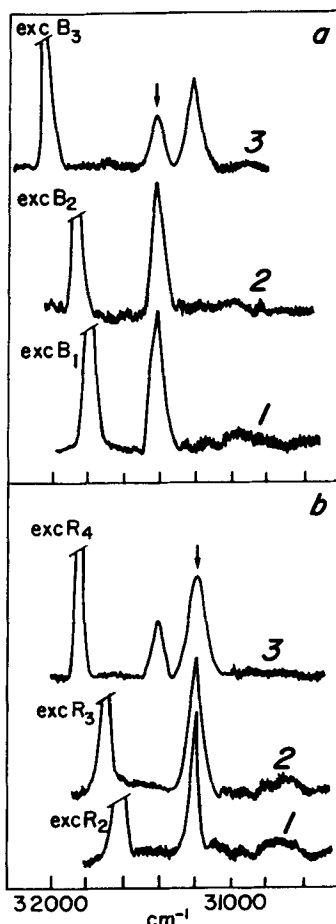


Figure 1. Fluorescence excitation spectrum of the 1-CNN:AN complex. The bands of the bare 1-CNN are noted (1) (2) ... with their respective frequencies. The bands labelled  $R_0, R_1, R_2, \dots$  and  $B_0, B_1, B_2, \dots$  refer respectively to the red-shifted and blue-shifted bands of the complex correlating with the main vibronic bands of 1-CNN. The 1-cyanonaphthalene sample was held at  $80^\circ\text{C}$  and the acetonitrile reservoir at  $-45^\circ\text{C}$ .

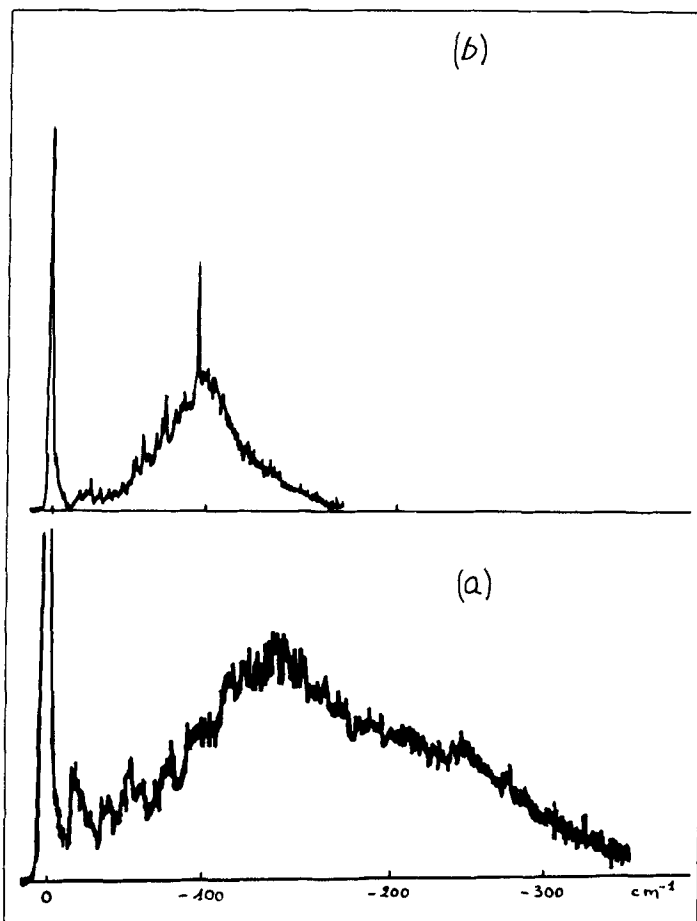


**Figure 2.** Dispersed emission spectra obtained by exciting the low lying vibronic bands of the 1-CNN:AN complex: (a) blue-shifted features excitation  $B_1$ ,  $B_2$ ,  $B_3$  corresponding to the 404, 454, 510  $\text{cm}^{-1}$  vibronic levels of 1-CNN; (b) red-shifted feature excitation  $R_2$ ,  $R_3$ ,  $R_4$  corresponding to the 454, 510 and 663  $\text{cm}^{-1}$  vibronic levels of 1-CNN. The spectral resolution is 30  $\text{cm}^{-1}$ .

the 1-CNN:DEE complexes where the threshold for isomerisation is less than 404  $\text{cm}^{-1}$ . The measured decay times are different for each isomer below the energy threshold and become identical for levels above the energy barrier. This observation indicates that a fast equilibrium is established between the two conformers before the relaxed fluorescence is emitted.

## 2.2 II-Complexes of 1-cyanonaphthalene with olefins

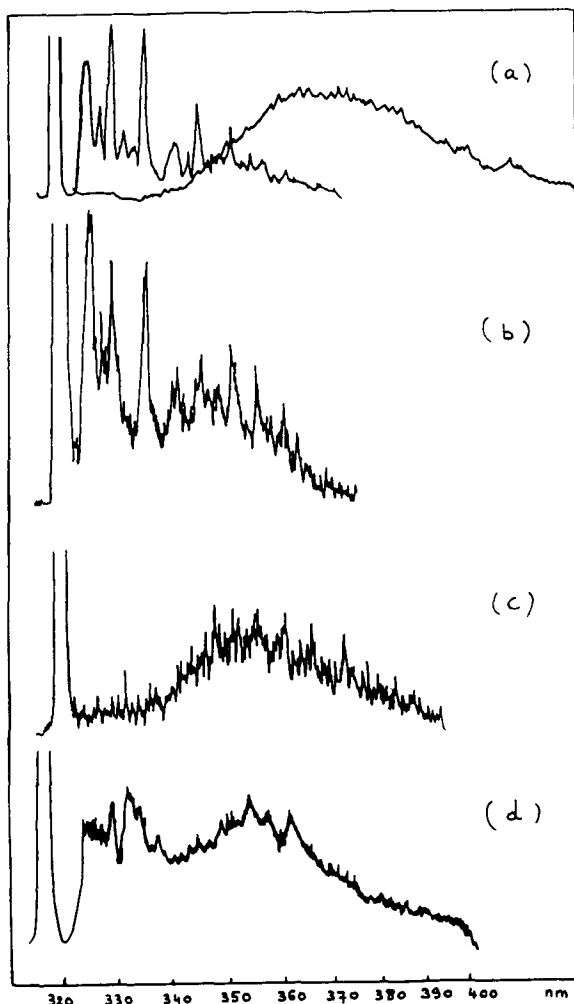
The fluorescence excitation spectra of the jet-cooled complexes of 1-CNN with 2,3-dimethyl-2-butene (DMB) and 2-methyl-2-butene (MB) are shown in figure 3. While the 1-CNN:DMB system exhibits a broad absorption band peaking at 150  $\text{cm}^{-1}$  of the monomer origin, the 1-CNN:MB complex gives rise to several narrow features superimposed on a broad band peaking at  $-100 \text{ cm}^{-1}$  from the 1-CNN 0-0



**Figure 3.** Fluorescence excitation spectra of jet-cooled 1-cyanonaphthalene complexes with: (a) 2,3-dimethyl-2-butene, (b) 2-methyl-2-butene. The 1-cyanonaphthalene sample was held at 80°C and 2,3-dimethyl-2-butene and 2-methyl-2-butene at  $-50$  and  $-70$ °C respectively.

transition. Dispersed fluorescence spectra obtained by exciting the broad feature at its maximum consist for both complexes of a continuous red-shifted fluorescence peaking respectively at 370 nm and 354 nm for 1-CNN:DMB and 1-CNN:MB. This type of emission spectra is characteristic of exciplex fluorescence and has been observed in the 1-CNN:DMB system in hexane solution. In the case of 1-CNN:MB system, excitation of the narrow feature at  $-96\text{ cm}^{-1}$  from the monomer origin gives rise to a structured spectrum similar to that of the 1-CNN  $0^0$  level. This type of emission is characteristic of weakly perturbed van der Waals complexes.

The 1-CNN:MB system thus presents simultaneously two types of absorption bands leading to different fluorescences. The dual properties of these complexes may be interpreted by the presence in the jet of two isomeric conformations of the complex. For one of these conformations, the 1-CNN singlet state is weakly perturbed by van der Waals interactions, while for the other conformation the locally excited state is strongly coupled to the charge transfer state (1-CNN $^-$ :MB $^+$ ). The different photo-



**Figure 4.** Emission spectra of jet-cooled 1-cyanonaphthalene complexes with: (a) 2,3-dimethyl-2-butene (resolution  $100\text{ cm}^{-1}$ , excitation at  $31\,250\text{ cm}^{-1}$ ). The figure shows also the bare 1-cyanonaphthalene  $0^0$  level emission (short wavelengths spectrum) recorded under the same conditions; (b) 2-methyl-2-butene (narrow band excitation at  $31\,304\text{ cm}^{-1}$ ); (c) 2-methyl-2-butene (broad band excitation at  $31\,300\text{ cm}^{-1}$ ); (d) 2-methyl-2-butene (narrow band excitation at  $31\,814\text{ cm}^{-1}$ ).

physical properties of the two isomeric forms reveals the importance of the relative orientation of the two partners of the complex for promoting the electron transfer process.

When the 1-CNN:MB van der Waals type isomer is excited with  $510\text{ cm}^{-1}$  vibrational energy, one obtains a double shaped fluorescence which can be divided into two components: a "blue" part peaking at the energy of the 0-0 transition of the initially excited complex and a "red" component similar to that attributed to the exciplex fluorescence. The "blue" emission corresponds to the relaxed emission expected after rapid intramolecular vibrational redistribution. As both conformers emit at this excess energy, it may be concluded that interconversion between the two

forms takes place with an energy barrier less than  $510\text{cm}^{-1}$  and that above the barrier both excited states are in equilibrium.

### **Conclusion**

This study has shown that 1-CNN van der Waals complexes can be trapped in several ground state conformations which may be distinguished in the excited state by their fluorescence properties. The presence of isomers in the jet may be related to specific local interactions at different sites of the 1-CNN molecule. Interconversion takes place between the excited conformers with an activation energy barrier.

### **References**

- Castella M, Millié P, Piuze F, Caillet J, Langlet J, Claverie P and Tramer A 1989 *J. Phys. Chem.* **93** 3941  
Gibson E M, Jones A C, Taylor A G, Bouvnan W G, Phillips D and Sandell J 1988 *J. Phys. Chem.* **92** 5449  
Levy D H 1980 *Annu. Rev. Chem.* **31** 197  
Levy D H 1986 *J. Chem. Soc. Faraday Trans.* **82** 1107  
Motyka A, Wittmeyer S A, Babbitt R J and Topp M R 1989 *J. Phys. Chem.* **93** 6322  
Piuze F and Tramer A 1990 *Chem. Phys. Lett.* **166** 503