

## Charge transfer and van der Waals states of jet-cooled dialkylaniline complexes with anthracene

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**Abstract.** We report here a study of the influence of a physical parameter (i.e. the ionization energy of different donor aromatic molecules) on the spectroscopic and dynamic properties of a series of molecular complexes A–D (A acceptor, D donor) where A is the anthracene molecule and D is one of the following dialkylanilines: dimethyl, diethyl, dipropyl or dibutyl. All complexes exhibit the same spectroscopic behavior already observed for dimethylaniline and diethylaniline cases and tentatively explained by the existence of two isomeric forms for each complex. Decay times and the broad band maximum frequency shifts for the exciplex-like emission type are experiencing a continuous variation in agreement with the change of the ionization energy of the donors. This is confirmed by calculations done using a very simple model based on the interactions between the diabatic  $A^*D$  and  $A^-D^+$  states of the complexes. This agreement is in favor of the initial assumption, that most physical parameters (complexation geometry, coupling between the diabatic states) are only weakly perturbed when changing the donor molecule and this despite an expected increased steric hindrance.

**Keywords.** Charge transfer state; van der Waals; dialkylaniline; anthracene; complexes.

### 1. Introduction

In our previous papers (Castella *et al* 1986a, b, 1989; Amirav *et al* 1988), we reported detailed spectroscopic data on molecular complexes AD of two aromatic molecules A and D (A acceptor – D donor) differing in their electron donor–acceptor properties. Their spectroscopic behavior could be roughly divided into two groups referred to as type I and type II:

—type I exhibits narrow band and structured fluorescence excitation spectra, resonant fluorescence with decay time identical to that of the bare A molecule. In this case the locally excited (LE) state is the lowest excited singlet state.

—type II characteristics are: broad and structureless excitation spectra, strongly red shifted and diffuse fluorescence with lifetimes longer by one order of magnitude than those of type I complexes, this emission is similar to that observed in solution for exciplexes. In this case the charge transfer state (CT) is located below the LE state.

Moreover for some complexes (perylene–N-methylaniline, anthracene–dimethylaniline and anthracene–diethylaniline) the excitation spectrum is composed of two overlapping spectral systems corresponding to types I and II. This behavior is explained by the existence of two isomeric forms of these complexes. These forms were tentatively assigned to two configurations, T-shaped and stacked respectively.

In the first isomeric form the emission takes place from the initially excited levels of the LE state, while in the latter one the emission arises from the CT state populated by a rapid relaxation of the LE state.

In order to obtain more complete information about this kind of systems, we extended our study to the complexes formed by different dialkylanilines: dimethyl(DMA), diethyl(DEA), dipropyl(DPA), dibutyl(DBA) with anthracene. One can expect that in this series of complexes most physical properties (binding energies, equilibrium geometries) are not very different. The varying parameter is the ionization energy of the donor, its variation should influence more strongly the spectroscopical and dynamical properties related to the charge transfer state such as the frequency and width of the broad band in the fluorescence excitation spectra and decay rate of type II emission, rather than the type I excitation and emission spectra. We report in the following a comparative study of the spectroscopic and dynamic properties of the four complexes.

## 2. Experimental and results

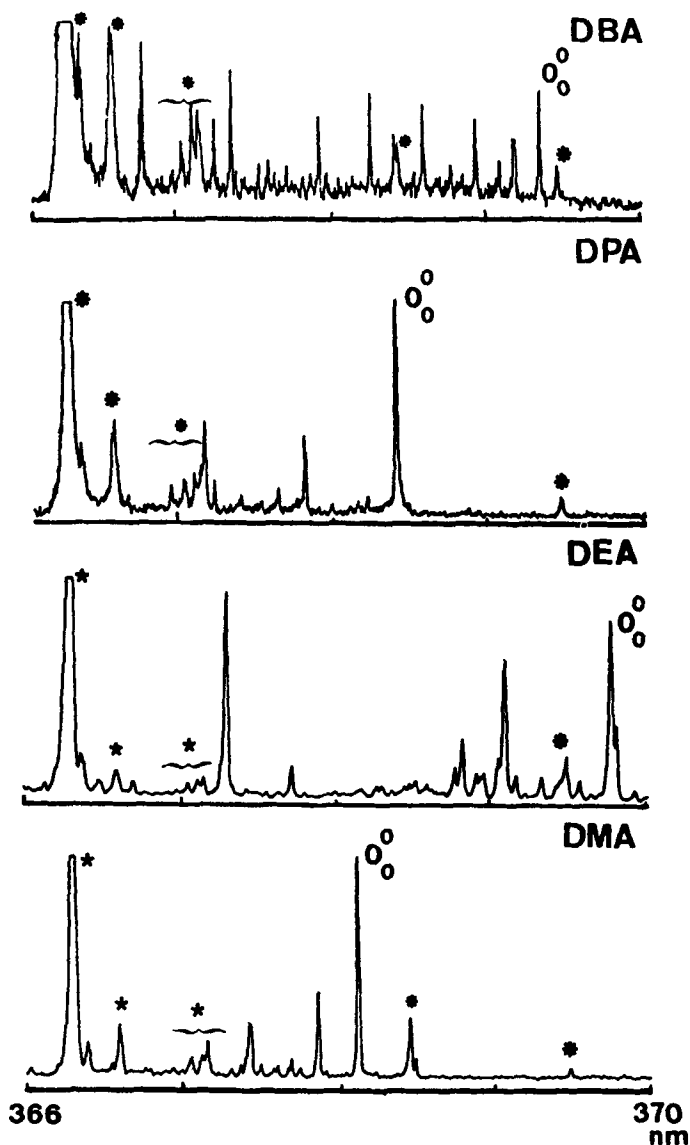
The experimental apparatus already described in Castella *et al* (1986a) is basically composed of a supersonic expansion crossed at right angles by a laser beam, the fluorescence detection axis being perpendicular to both laser and expansion axes. The dialkylanilines (heated to a suitable temperature in order to approach 1-1 stoichiometry with anthracene) were seeded in helium ( $P = 2-3.5$  bar) and allowed to expand through a  $100\ \mu\text{m}$  nozzle. The adducts formed were excited by a Lambda Physik excimer pumped dye laser in the spectral domain corresponding to the origin of the  $A^* \leftarrow A$  transition of the bare anthracene. The bands corresponding to type I and type II fluorescence components appeared in distinct spectral domains (365-420 nm and 420-520 nm respectively), the fluorescence excitation spectra were recorded using a low resolution Bausch and Lomb monochromator with a 10 nm bandpass centered around respectively 370 and 450 nm. Decay curves were recorded and averaged by a Lecroy 6880 transient recorder, lifetime determination was done using a classical least squares curve fitting program.

### 2.1 Type I

The fluorescence excitation spectra in the 366-370 nm spectral range containing the complexes  $O_0^0$  vibronic transition recorded with detection centered in the type I emission domain are presented in figure 1 and the strongest bands frequencies are listed in table 1. From these experimental data we notice that:

- (i) each spectrum is structured, composed of narrow bands and has an origin red shifted with respect to the  $O_0^0$  band of the  $A^* \leftarrow A$  transition in free anthracene;
- (ii) the origin red shift variation is not directly correlated to the ionization energy change of the donor (see table 2) but is more likely alkyl group specific;
- (iii) intermolecular mode patterns are very different and no extrapolation is possible between complexes. Moreover in the DBA-anthracene case the spectrum exhibits a complicated structure and a different band intensity pattern (i.e. the first band is not the most intense as it is the case for the other donors) which may be accounted for by a more important change in the potential surface of the LE state with respect to the ground state (responsible for an increased anharmonicity).

Besides, the decay times measured at the origin for each complex are equal to that of the bare molecule ( $25 \pm 5$  ns).



**Figure 1.** Fluorescence excitation spectra of anthracene complexes with DMA, DEA, DPA, and DBA detected in the  $370 \pm 10$  nm spectral region. The anthracene hot bands are marked with an asterisk.

In conclusion it appears that these spectra and decay times are not essentially different from those of complexes where the LE state is well separated from the CT state.

## 2.2 Type II

The fluorescence excitation spectra corresponding to the type II emission are given in figure 2, while the shift of the broad band maximum frequency and the lifetimes measured at these frequencies, are listed in table 2. All spectra have a common aspect,

**Table 1.** Frequencies of the strongest band:  $\nu$  ( $\text{cm}^{-1}$ ), intervals:  $\delta\nu$  ( $\text{dm}^{-1}$ ), relative intensities in the narrow band (type I) system of the fluorescence excitation spectrum of the anthracene complexes with DMA, DEA, DPA and DBA in the 366–370 spectral domain corresponding to their  $0_0^0$  band.

$\nu$	$\delta\nu$	$I$	$\nu$	$\delta\nu$	$I$
<i>DMA</i>			<i>DPA</i>		
27164.5	0.0	10.0	27144.0	0	10.0
27183.5	19.0	2.5	27158.0	14	0.5
27195.0	30.5	1.5	27188.0	44	30.0
27216.0	50.5	1.5	27200.0	56	0.7
			27218.0	74	0.5
			27230.0	86	0.8
			27234.0	90	4.0
			27251.0	107	0.7
			27278.0	134	4.0
$\nu$	$\delta\nu$	$I$	$\nu$	$\delta\nu$	$I$
<i>DEA</i>			<i>DBA</i>		
27040.0	-2.5	5.0	27073.0	0.0	7.0
27042.5	0.0	10.0	27085.5	12.5	4.0
27063.0	20.5	2.0	27093.0	20.0	1.5
27067.5	24.5	1.3	27104.5	31.5	5.0
27075.5	32.5	1.5	27130.0	57.0	6.0
27087.0	44.5	1.5	27144.0	71.0	4.0
27092.0	49.5	12.5	27155.0	82.0	7.0
27095.5	53.0	4.0	27179.5	106.5	5.0
27102.5	60.0	1.5	27220.5	147.5	8.0
27112.5	70.0	4.5	27229.0	156.0	5.0
27116.5	74.0	0.2	27263.5	190.5	10.0
27122.0	79.5	0.1			

with only slight differences between them. From these experimental data it is apparent that the four complexes share the following common features:

- (i) strong, broad, non-structured and red shifted emission;
- (ii) longer lifetimes compared to type I case;
- (iii) a second less intense and less red shifted broad non-structured emission. The shift between the maximum of these two broad bands is always the same and equal to  $385 \text{ cm}^{-1}$  which is the value of one quantum of the  $\nu_7$  vibration of bare anthracene.

Moreover for the anthracene-DMA, anthracene-DEA and anthracene-DPA complexes the same narrow band system observed in the type I excitation spectra is superimposed on the broad band red-side wing. This occurrence was previously studied in detail for DMA and DEA cases (Piuzzi and Tramer 1990) and explained by the existence of two isomeric forms. Excitation of the form responsible for the narrow features is followed by:

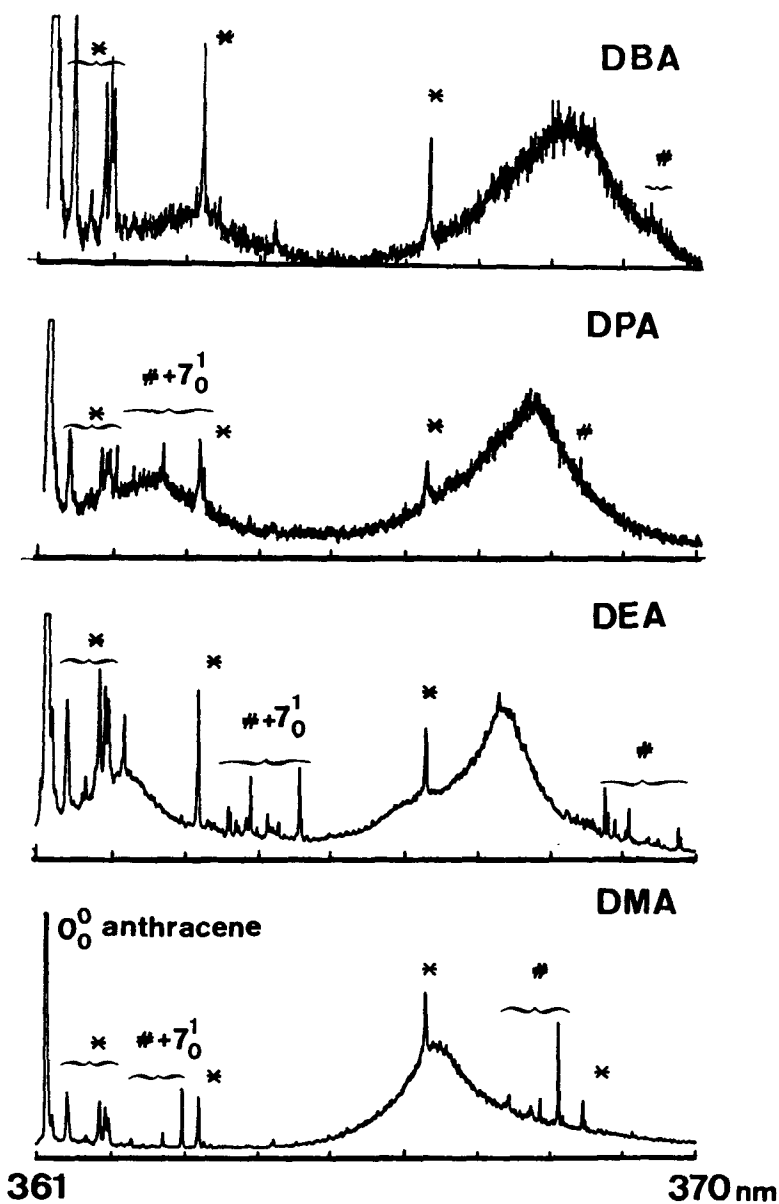
- (i) resonant emission from the same form (type I), or;
- (ii) electronic relaxation leading to the other configuration with subsequent emission

**Table 2.** Experimental and calculated red shifts of: (i) the origin of the narrow band system ( $\delta\nu$  type I), (ii) the maximum of the broad band ( $\delta\nu$  type II), and the measured and calculated decay time measured at the frequency of the maximum of the broad band.

Complex A - C <sub>6</sub> H <sub>5</sub> NR <sub>2</sub> with R =	I <sub>D</sub> (eV)	$\delta\nu$ type I emission (cm <sup>-1</sup> ) (experimental)	$\delta\nu$ type II emission (cm <sup>-1</sup> ) (experimental)	$\delta\nu$ type II emission calculated values (cm <sup>-1</sup> ) with V =		$\tau$ type II emission (ns) (experimental)	$\tau$ type II emission calculated values (ns) with V =	
				700 cm <sup>-1</sup>	900 cm <sup>-1</sup>		700 cm <sup>-1</sup>	900 cm <sup>-1</sup>
				(experimental)	(experimental)		(experimental)	(experimental)
CH <sub>3</sub>	7.12 ± 0.03	523	400	—	—	250	309	234
C <sub>2</sub> H <sub>5</sub>	6.98	646	470	428	448	265	366	304
C <sub>3</sub> H <sub>7</sub>	6.93	541	500	435	460	305	381	323
C <sub>4</sub> H <sub>9</sub>	6.87*	613 ± 3	530 ± 10	—	—	350 ± 25	—	—

The ionization energies of the donors come from Lias *et al.* (1985). The values for DEA and DPA have been measured by the charge transfer technique. Their values have been determined according to the DMA value which is the only one known with good precision (Akopyan and Vilesov 1964).

\* The DBA value is only a tentative extrapolated value, this value is not given (Lias *et al.* 1985) and the only value available comes from a series which shows discrepancies with the DEA and DPA values.



**Figure 2.** Fluorescence excitation spectra of anthracene complexes with DMA, DEA, DPA, and DBA detected in the  $450 \pm 10$  nm spectral region where type II fluorescence appears. The anthracene hot bands are marked with an asterisk. The overlapping narrow band system is marked with a #.

(type II). In the anthracene-DBA complex either the signal to noise ratio or a change in physical properties (i.e. isomerization potential barrier) impedes the observation of the overlapping narrow band system, but the presence of a non-resolved shoulder at the frequency position of the corresponding narrow band system accounts for the latter explanation.

The slightly varying characteristics deduced from the experimental results are:

- (i) the frequency of the broad band maximum is continuously red-shifted when changing from CH<sub>3</sub> to the C<sub>4</sub>H<sub>9</sub> alkyl groups;
- (ii) the decay times measured at the broad band maximum frequency are continuously increasing with decreasing ionization energy of the donor;
- (iii) the width and shape of the broad band are changing but remain difficult to correlate with any physical parameter variation.

These results indicate that the four complexes studied here have a behavior which is roughly the same, and this despite an expected increasing steric hindrance effect when changing alkyl groups from CH<sub>3</sub> to C<sub>4</sub>H<sub>9</sub>.

### 3. Discussion

These above observations suggest that there exists a trend towards an increase in the broad band frequency red shift as well as in the emission lifetimes when the ionization energy of the dialkylaniline is decreasing while no direct effect is observed in the case of type I emissions which are related to the LE state. Moreover, the frequency shift of the broad band maximum is proportional to the ionization energy (IE) variation. In order to explain these experimental observations we propose here to use a previously proposed simplistic model (Amirav *et al* 1988; Castella *et al* 1989).

We suppose that the energies  $E_{CT}$  and  $E_{LE}$  and wavefunctions  $|CT\rangle$  and  $|LE\rangle$  of the adiabatic CT and LE states result from the interaction between zero-order (diabatic) states: A\*D (van der Waals state) and A<sup>-</sup>D<sup>+</sup> (ionic) states with energies  $\varepsilon_{vdW}$  and  $\varepsilon_{ion}$ , respectively. As we assume that most physical parameters are only weakly perturbed when changing donors, we make the approximation that the energy of the first excited van der Waals state ( $\varepsilon_{vdW}$ ) is the same for all complexes, while that of the ionic state depends on the ionization potential of the donor following to the well-known formula:

$$\varepsilon_{ion} = a + I_D \quad (1)$$

where  $a$  is a constant determined by the electron affinity of the acceptor (EA) and interaction energy between the ion pair.

The adiabatic states  $E_{LE}$  and  $E_{CT}$  are coupled by the matrix element  $V$  (supposed to be the same for all complexes) and since for these complexes,  $\varepsilon_{ion} < \varepsilon_{vdW}$ , this implies  $E_{CT} < E_{LE}$  with energies:

$$E_{LE,CT} = \frac{1}{2}(\varepsilon_{ion} + \varepsilon_{vdW}) \pm \frac{1}{2}(\delta\varepsilon^2 + 4V^2)^{\frac{1}{2}}, \quad (2)$$

where  $\delta\varepsilon = \varepsilon_{vdW} - \varepsilon_{ion}$  with  $\delta E = E_{LE} - E_{CT} = (\delta\varepsilon^2 + 4V^2)^{\frac{1}{2}}$ , and the following wave functions:

$$|CT\rangle = \alpha|vdW\rangle + \beta|ion\rangle, \quad |LE\rangle = -\beta|vdW\rangle + \alpha|ion\rangle, \quad (3)$$

where  $\alpha = V/\delta\varepsilon$  and  $\beta \cong 1$ . Hence, from the transition probabilities between the ground and CT state we obtain:

$$k_{0-CT} = \alpha^2 k_{0-vdW} + \beta^2 k_{0-ion} \quad (4)$$

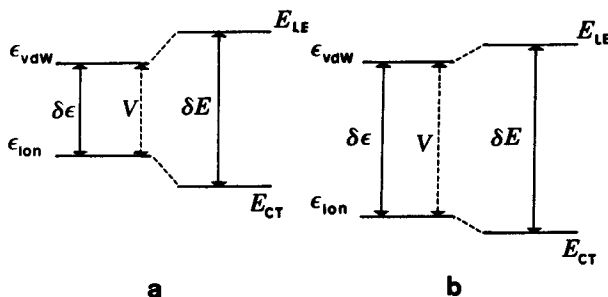


Figure 3. (a) Diagram representing the relations between the different terms used by the model treatment. (b) Same diagram but for another donor molecule with lower ionization energy where  $\epsilon_{vdW}$  is supposed to be the same as in case (a) while  $\epsilon_{ion}$  is lower.

where  $k_{0-CT}$ ,  $k_{0-vdW}$ ,  $k_{0-ion}$  are the radiative constants for the charge-transfer and adiabatic van der Waals and ionic states respectively.

The experimental data for a series of alkyylaniline-hydrocarbon complexes show that  $k_{0-vdW}$  is practically the same as that of the bare hydrocarbon molecule (ca.  $4 \times 10^7 \text{ s}^{-1}$  for anthracene), while  $k_{0-ion}$  is significantly lower, of the order of  $2 \times 10^6 \text{ s}^{-1}$ .

As can be easily seen (figure 3), the decrease of the ionization potential of the donor results in the lowering of  $\epsilon_{CT}$  which corresponds to an increase of the  $\delta\epsilon$  value. This implies in turn a weaker mixing between ionic and van der Waals states i.e.:

- (i) a depression of  $E_{CT}$  (an appreciable variation of the type II fluorescence band red shift's)
- (ii) a small decrease of  $E_{LE}$  (a small variation of the  $O_0^0$  band frequency in the fluorescence excitation spectrum belonging to the type I emission) and
- (iii) a reduction of  $k_{0-CT}$  (increase of the fluorescence decay time).

All these effects are observed (except for type I emissions where variations are not correlated). If the previously proposed value of  $V \cong 700 \text{ cm}^{-1}$  (Amirav *et al* 1988) is assumed, we obtain from the observed value of  $\delta E = 4100 \text{ cm}^{-1}$  for the DMA complex a calculated value of  $\delta\epsilon_{DMA} \cong 3850 \text{ cm}^{-1}$  and for the other complexes:

$$\delta\epsilon_D = \delta\epsilon_{DMA} - I_{DMA} + I_D. \quad (5)$$

The frequency shifts and lifetime changes estimated in this way are of the right order of magnitude and in agreement with experimental data in spite of using an extremely simplistic model. The calculated values are listed in table 2 together with the experimental data, using the values of 700 and  $900 \text{ cm}^{-1}$  for the coupling potential  $V$ . No calculated data are listed for the DBA complex due to the uncertainty of the ionization energy of DBA. For both series of calculated data an agreement with the experimental data variation is obtained. The  $900 \text{ cm}^{-1}$  gives a better agreement with the measured decay times.

The fact that, even with a very simple model and using rough approximations, it is possible to reproduce the observed variation for all complexes confirms that most physical parameters (binding energies, equilibrium geometries, coupling the  $A^*D$  and  $A^-D^+$ ) are similar for the series of anthracene-dialkyylaniline complexes, in agreement with the initial assumption. In order to better understand the processes involved in



the intermolecular mode pattern changes (group specificity, isomerization, ...) for the form of the complexes giving typical van der Waals emission (type I) more work is necessary. For the isomeric form giving exciplex-like emission (type II) better values of the ionization energies of the dialkylanilines and use of a more refined model could enhance the agreement between experimental and calculated data.

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