110. Multiple Charge-Transfer Transitions in Alkylbenzene-TCNE Complexes[1])

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(11. II. 76)

Summary. Several alkylbenzene-TCNE complexes are reinvestigated, yielding improved ground state thermodynamic parameters. The effect of competing solvent complexation with the acceptor is also considered. The experimental CT-band profiles for the complexes in solution and in the gas phase are deconvoluted into two (theoretically expected) CT-subbands, furnishing accurate energies of the first and second CT-state of the systems. Comparison with the corresponding donor IP's leads to insight into the preferred ground state conformation of the complexes. The thermodynamics of ionic photodissociation of the complexes is evaluated as a function of solvation and the results compared with recent experimental work.

Introduction. – Photoelectron Spectroscopy (PES.) on donor systems **D** yields accurate information about the energy levels of $\mathbf{D}^+$. It provides therefore an opportunity to compare with the energy levels of charge-transfer (CT)-states $\mathbf{D}^+\mathbf{A}^-$ of excited molecular complexes **DA**, where **A** is some acceptor system. In an attempt to resolve the question whether multiple CT-bands arise from transitions from several occupied orbitals of **D** to a single empty orbital of **A**, or *vice versa, Aloisi et al.* [1] have pioneered such correlations for a number of complexes, involving various aromatic and heteroaromatic **D**'s, where two CT-bands are clearly discernible.

Such bands have usually a broad structureless appearance both for the complex in solution or in the gas phase. Since moreover the two band maxima are in most cases within 1 eV distant from each other, the question arises if the $\tilde{\nu}_{\text{max}}$-values are good representatives for the vertical transition energies $\tilde{\nu}_{\text{V}}$. At any rate, such correlations are impossible in cases where only one band appears, even though theory predicts the existence of two non-degenerate low lying CT-states.

In the course of a general program in which correlations between PES- and CT-data are attempted, we reexamined the CT-spectra of benzene **1** and its alkyl derivatives **2**–**7** with TCNE. An accurate establishment of the $\tilde{\nu}_{\text{V}}$-values was achieved by the deconvolution technique described below, both for the solution and the gas phase.


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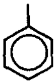
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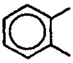
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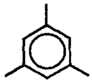
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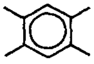
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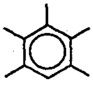
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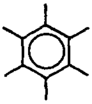
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[1]) Part 2 of the series: 'Weak molecular complexes with hydrocarbon donors'. Part 1: [31].

As a necessary prerequisite the thermodynamic parameters of the association reaction

$$\mathbf{D} + \mathbf{A} \underset{}{\overset{K}{\rightleftarrows}} \mathbf{DA} \tag{1}$$

were reestablished for the solution phase under more elaborate experimental conditions as before. TCNE (symbol **A**) as acceptor and CH_2Cl_2 as solvent were chosen.

Results and discussion. – *Complexes in solution.* The optical density of the solutions of **D** and **A** (seven solutions for each **D**) were recorded on a *Unicam* SP-800 D spectrophotometer. The data were subjected to the standard *Benesi-Hildebrand* (*B-H*) treatment, employing a least squares procedure. This led to error limits $\varepsilon_+, \varepsilon_-$ for the extinction coefficients ε, corresponding to the standard deviations σ of the intercept c in the *B-H*-plots. Since σ(m) of the slope m was found two to three orders of magnitude smaller than σ(c), the apparent K_{ap}-values and their error limits were calculated by

$$K_{ap} = \frac{1}{m\varepsilon}, \quad K_{ap\mp} = \frac{1}{m\varepsilon_\pm} \tag{2}$$

For the determination of $\Delta H^0_{ap}(l)$ it was assumed that ε is constant in the temperature range 0° to 25°, thus avoiding the separation of K_{ap} and ε at a given temperature. Hence, the temperature dependence of m in (2) led directly to $\Delta H^0_{ap}(l)$. The measurements were carried out at 0°, 10° and 25°.

The results displayed in Tab. 1 exhibit marked differences with respect to those reported for the same series in [2]. This concerns the extinction coefficients and therefore also the equilibrium constants. The differences are well outside our error range. Important is the outcome that our $\Delta H^0_{ap}(l)$-values are constantly smaller than the reported ones. Appreciating the delicacy of the matter, we believe that our results are presumably more adequate than those reported earlier [2] since we employed more elaborate experimental conditions which can be summarized as follows:

- more measurements at a given temperature,
- more measurements for the temperature dependence,
- temperatures well below the boiling point of the solvent,
- numerical analysis.

We also note the good agreement between our values for **1A** and **4A** and those reported in [3].

Strong evidence has recently accumulated that association constants determined by the present procedure are only apparent ones (K_{ap}) and do not correspond to the true ones (K_1) of (1) [4]. Two factors are mainly responsible for this: a) termolecular associations of type $\mathbf{D_2A}$ (constant K_2) [5], and b) solvent-acceptor competition associations (constant K_s) [3].

From the data given in [6] which are relevant to our series it follows that K_1 is only marginally larger than K_{ap}. Though effect b) has not been included explicitly

Tab. 1. *Spectroscopic and thermodynamic parameters* (based on ${}^{c}K_{ap}$-constants) *of TCNE-benzene complexes in CH_2Cl_2 at 25°* (see text for explanation of symbols)

TCNE-complex	${}^{x}K_{ap}^{25°}$ (${}^{x}K_{ap}^{22°}$ of [2])	$\varepsilon_-, \underline{\varepsilon}, \varepsilon_+$ (ε of [2]) $\ell\ mol^{-1}\ cm^{-1}$	$-\Delta H_{ap}^{0}(\ell)$ ($-\Delta H^{0}(\ell)$ of [2]) kcal mol^{-1}	$-\Delta S_{ap}^{0}(\ell)$ cal K^{-1} mol^{-1}	$-\Delta G_{1}^{0}(\ell)$ [1] kcal mol^{-1}	$-\Delta H_{1}^{0}(\ell)$ [2] kcal mol^{-1}	$-\Delta S_{1}^{0}(\ell)$ [3] cal mol^{-1} K^{-1}
1	2.08 (2.00)	2930, $\underline{3310}$, 3800 (3840)	1.63 (2.30)	9.46	0.46	4.01	11.91
2	4.67 (3.70)	$\underline{2680}$ (4060)	2.34 (2.72)	10.26	0.94	4.72	12.71
3a	12.31 (7.64)	1680, $\underline{1710}$, 1750 (4600)	3.08 (3.37)	10.80	1.51	5.46	13.25
3b	11.26 (6.97)	2345, $\underline{2510}$, 2690 (4300)	2.84 (----)	10.17	1.46	5.22	12.62
4	21.85 (17.3)	2320, $\underline{2600}$, 2950 (4610)	3.97 (4.52)	12.65	1.85	6.35	15.10
5	38.9 (54.2)	2940, $\underline{2960}$, 2970 (4800)	4.17 (5.07)	12.18	2.19	6.55	14.63
6	105.5 (123.0)	3720, $\underline{3920}$, 4140 (5200)	5.27 (6.97)	13.92	2.77	7.65	16.37
7	301.7 (263.0)	4130, $\underline{4240}$, 4350 (5450)	6.06 (----)	14.47	3.40	8.44	16.92

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[1] $\Delta G_1^0(l) = \Delta G_{ap}^0(l) - 0.03$, see text.

[2] $\Delta H_1^0(l) = \Delta H_{ap}^0(l) - 2.38$, see text.

[3] $\Delta S_1^0(l) = \Delta S_{ap}^0(l) - 2.45$.

in [5], solvent competition is not likely to change the above relationship since non-polar solvents were used. It follows that considering only a) $\Delta G_1^\circ(l) \approx \Delta G_{ap}^\circ(l)$ is a good approximation for the present series. Furthermore, since $K_1/K_2 \approx 10$, whereas for the corresponding extinction coefficients $\varepsilon_1/\varepsilon_2 \approx 0.5$, variations of the optical density of the complex solutions as a function of temperature will be overwhelmingly determined by changes in the bimolecular complex concentration. As a result $\Delta H_1^\circ(l) \approx \Delta H_{ap}^\circ(l)$ follows. Unfortunately this cannot be verified since no temperature dependence studies of K_1, K_2 have as yet been undertaken.

Taking into account only solvent competition (effect b), *e.g.* ignoring a), and making the usual *B-H*-approximation yields [3]

$$K_1 = K_{ap}\,(1 + K_s[\mathbf{S}]_0) \tag{3}$$

with $[\mathbf{S}]_0$ being the molar concentration of the pure solvent ($[\mathbf{S}]_0 = 15.62$ mol l^{-1} for CH_2Cl_2 at 25°)[2]). Use of the data for K_s provided in [3] or [7] yields

$$\Delta G_1^\circ(l) = \Delta G_{ap}^\circ(l) - 1.65 \text{ kcal mol}^{-1}. \tag{5}$$

For later comparisons with gas phase results, use of ${}^cK_{ap}$-instead of ${}^xK_{ap}$-constants [4] leads to

$$\Delta G_1^\circ(l) = \Delta G_{ap}^\circ(l) - 1.65 \text{ kcal mol}^{-1} + 1.62 \text{ kcal mol}^{-1}, \tag{5a}$$

listed in Tab. 1.

For an estimate of $\Delta H_1^\circ(l)$ from $\Delta H_{ap}^\circ(l)$ consider (6) as obtained from (3):

$$K_1 = K_{ap}\,K_s[\mathbf{S}]_0\,(1 + K_s^{-1}[\mathbf{S}]_0^{-1}) \tag{6}$$

Since $K_s^{-1}[\mathbf{S}]_0^{-1} \ll 1$, $\ln(1 + K_s^{-1}[\mathbf{S}]_0^{-1}) \approx K_s^{-1}[\mathbf{S}]_0^{-1}$ follows.

On this basis we arrive at

$$\Delta H_1(l) \approx \Delta H_{ap}^\circ(l) + \Delta H_s^\circ(l) - \frac{RT^2}{[\mathbf{S}]_0}\left((1 - K_s^{-1}[\mathbf{S}]_0^{-1})\frac{d[\mathbf{S}]_0}{dT} + K_s^{-2}\frac{dK_s}{dT}\right). \tag{7}$$

For $d[\mathbf{S}]_0/dT$ and dK_s/dT the values $3.34 \cdot 10^{-4}$ mol l^{-1} K^{-1} and $-1.4 \cdot 10^{-2}$ l mol^{-1} K^{-1}, resp. could be extracted from [8] and [3], resp. Hence

$$\Delta H_1^\circ(l) \approx \Delta H_{ap}^\circ(l) + \Delta H_s^\circ(l) + 0.17 \text{ kcal mol}^{-1}. \tag{8}$$

With $\Delta H_s^\circ(l) = -2.55$ kcal mol^{-1} [3] we finally arrive at

$$\Delta H_1^\circ(l) \approx \Delta H_{ap}^\circ(l) - 2.38 \text{ kcal mol}^{-1}. \tag{9}$$

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[2]) Within the *Benesi-Hildebrand* approximation simultaneous consideration of a) and b) yields

$$K_1 = K_{ap}\,(1 + K_1K_2[\mathbf{D}]^2 + K_s[\mathbf{S}]_0) \tag{4}$$

with $[\mathbf{D}]$ being the concentration of the donor. No analysis according to (4) has as yet been undertaken.

In Tab. 1 these values are listed for the present complexes. Comparison with $\Delta H_1^\circ(l)$ for the complexes **1A** and **4A**, obtained in [3] by direct measurement, indicates that the treatment (6)–(9) is indeed satisfactory.

Complexes in the gas phase. The gas phase spectra of some alkylbenzene-TCNE complexes are displayed in [9] [10]. These figures were photographically enlarged and analysed. The thermodynamic parameters were taken from [9] [10]. Note the similarity of $\Delta H_1^\circ(l)$ and $\Delta S_1^\circ(l)$ of Tab. 1 with the corresponding values in [9] for the gas phase. In earlier work [9] $\Delta H_{ap}^\circ(l)$-values were compared with the gas phase parameters and the marked differences discussed on the basis of solvation of the equilibrium partners in (1). The present results suggest that these differences are merely due to the interference of the solvent-acceptor equilibrium.

Vertical CT-energies after deconvolution of spectra. Since the precision of the *Cary* Spectrophotometer employed in [2] is known to be greater than the presently used apparatus, the energetic analysis of the solution spectra was based on the $\tilde{\nu}_{max}$-values reported therein.

It has been found [11] that CT-bands can well be represented by asymmetric *Gaussians* [12], defined by the four parameter equation

$$Y(X) = Y_0 \exp(-\ln 2\, [\ln\{1 + 2B(X-X_0\}/D)/B]^2 \qquad (10)$$

with

B = asymmetry parameter
D = half width
X_0 = position of maximum
Y_0 = amplitude of maximum.

Such functions were fitted to the CT-bands of the complexes of **1**, **4** and **7**³), assuming that here the two visualizable CT-states are nearly degenerate⁴).

For the other complexes the degeneracy of the radical cation states is removed by the reduced symmetry of **D**. Here, two separated CT-bands can in principle be expected and are also indicated in the spectra of some complexes as noted already earlier. For the deconvolution of the observed bands into two subbands the following assumptions were made:

- within one complex, B and D for the two CT-bands are equal,
- within the series, B and D vary monotonically with ΔH_1°. This assumption has its basis in the fact that, the stronger the complex, the larger will be the curvature of the ground state potential energy curve. As a result the *Franck-Condon* profile of the CT-bands is expected to become narrower. For the gas phase a linear function had to be taken since B and D from only two reference complexes (*i.e.* **1A**, **4A**) are known. For the solution phase with three reference systems (**1A**, **4A**, **7A**), a parabolic dependence of B and D from $\Delta H_1^\circ(l)$ was chosen.

The resulting B- and D-values are displayed in Tab. 2 and Tab. 3 for gas- and solution phase, resp. They allow a decomposition of the experimental CT-bands into two subbands, employing a trial and error procedure for the two disposable parameters X_0 and Y_0 in (10). The optimal values for the band position of the two CT-bands

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³) Done for solution spectrum only, since gas phase spectrum not displayed in literature.

⁴) Though the ground states of $\mathbf{1}^+$, $\mathbf{4}^+$ and $\mathbf{7}^+$ are degenerate (neglecting *Jahn-Teller* effects), this may not be so in the CT-states $\mathbf{1}^+\mathbf{A}^-$, $\mathbf{4}^+\mathbf{A}^-$ and $\mathbf{7}^+\mathbf{A}^-$, since the symmetry of the complex is reduced by the presence of TCNE. A possible splitting, however, is certainly small.

$X_0^1 = \tilde{\nu}_v^1$, $X_0^2 = \tilde{\nu}_v^2$, as well as the ratio of intensities Y_0^1/Y_0^2 are given in Tab. 4 (gas phase) and Tab. 5 (solution phase). They are compared with earlier results. The deconvoluted solution spectra are displayed in Fig. 1.

Tab. 2. *Enthalpy of formation of gas phase TCNE-benzene complexes from literature; deconvolution parameters B and D for gas phase CT-spectra* (see text)

TCNE-complex	$-\Delta H^0$(g) (kcal mol^{-1})	B	D (cm^{-1})
1 a)	6.6 c) [10]	0.3365	5645
4 a)	9.9 d) [9]	0.36	5300
2	7.22 c) [10]	0.341	5580
3a	8.10 d) [9]	0.347	5485
3b	8.40 c) [10]	0.350	5440
5	10.8 d) [9]	0.366	5200
7 b)	~13	--	--

a) Scaling complexes, assuming two degenerate CT-states (see text).

b) No spectrum, only $\tilde{\nu}_v$ published; ΔH° (g) (**7A**) extrapolated from ΔH° (g) (**1A**) and ΔH° (g) (**4A**).

c) T = 298.16 K

d) T = 398.16 K

Tab. 3. *Enthalpy of formation* (25°) *of TCNE-benzene complexes in CH_2Cl_2-solution; deconvolution parameters B and D of solution phase spectra* (see text)

TCNE-complex	$-\Delta H_1^0(\ell)$ (kcal mol^{-1})	B	D (cm^{-1})
1 a)	4.01	0.371	5865
4 a)	6.35	0.250	5500
7 a)	8.44	0.154	5310
2	4.72	0.332	5735
3a	5.46	0.297	5615
3b	5.22	0.328	5720
5	6.55	0.244	5470
6	7.65	0.191	5360

a) Scaling complexes, assuming two degenerate CT-transitions

Tab. 4. *Vertical CT-transition energies from deconvoluted spectra of gas phase complexes; vertical ionization potentials*

TCNE-complex	$\tilde{\nu}_v^1$ $\tilde{\nu}_v^2$ (Lit.) in cm^{-1}	Y_0^1/Y_0^2	IP_v^1 IP_v^2 in eV a)
1	28950 (28950 [10])	–	9.25
2	25850 27800 (27030 [9], 27100 [10])	1.12	8.78 9.00
3a	23050 27800 (23530 26880 [9])	1.39	8.37 9.05
3b	24270 26570 (25390 [10])	1.54	8.45 8.90
4	23640 (23640 [9])	-	8.42
5	20750 24350 (21140 23260 [9])	1.75	8.10 8.60
7	19690 (19690 [9])	-	7.86

a) From [13].

Tab. 5. *Vertical CT-transition energies from deconvoluted spectra of solution phase complexes; red shift with respect to gas phase transitions*

TCNE-complex	$\tilde{\nu}_v^1$ $\tilde{\nu}_v^2$ (Lit.)[a] in cm^{-1}	Y_0^1/Y_0^2	$\delta\tilde{\nu}_v^i = \tilde{\nu}_{v,gas}^i - \tilde{\nu}_{v,sol}^i$ $i = {1 \atop 2}$
1	26040 (26040)	---	2910
2	23530 25330 (24630)	1.08	2550 2700
3a	21450 (21740) 25800 (24100)	1.61	1600 2000
3b	22100 23850 (23260)	0.94	2170 2720
4	21690 (21690)	---	1950
5	19200 22700 (20830)	1.58	1550 1650
6 [b]	18330 19730 (19230)	0.77	---
7	18350 (18350)	---	1340

[a] Ref. [2].

[b] $IP_v^1 = 8.00$ eV, $IP_v^2 = 8.30$ eV [13]; other $IP_{v}'s$ in Tab. 4.

For **2A** and **3bA** in the gas phase, the earlier analysis in [9] and [10] revealed only one CT-band. The present procedure, however, led to the establishment of two CT-transitions – as theoretically expected – with sizeable energy separations of 2000 cm^{-1} and 2300 cm^{-1}, resp. For **3aA** and **5A** two transitions were noted earlier [9] [10]. The reported ν_{max}-values, however, deviate significantly from those obtained by deconvolution ($\tilde{\nu}_v$). As a result, the present energy separation of the CT-states are $\Delta\tilde{\nu}_v(\mathbf{3aA}) = 4750$ cm^{-1} and $\Delta\tilde{\nu}_v(\mathbf{5A}) = 3600$ cm^{-1}, to be compared with $\Delta\tilde{\nu}_{max}(\mathbf{3aA}) = 3550$ cm^{-1} and $\Delta\nu_{max}(\mathbf{5A}) = 2120$ cm^{-1} of [9].

Similar improvements were achieved for the solution spectra. Here, for **2A**, **3bA** and **5A** the position of the individual CT-bands could be established. For **3aA**, the earlier reported $\tilde{\nu}_{max}$-values for the two CT-bands led to a splitting of the CT-states of $\Delta\tilde{\nu}_{max} = 2360$ cm^{-1} [2]. The present technique leads to $\Delta\tilde{\nu}_v = 4350$ cm^{-1}, *i.e.* to an increase in energy splitting of 0.25 eV!

Correlation between ionization potentials and CT-excitation energies. According to the theory of weak molecular complexes [14] the relationship between IP_v of **D** and $h\nu_v$ is given by

$$h\nu_v = IP_v - c_1 + c_2\,(IP_v - c_1)^{-1} \tag{11}$$

with c_1, c_2 being positive constants. For a limited range of IP_v-values the hyperbolic equation (11) can be approximated by the linear one

$$h\nu_v = aIP_v - b. \tag{12}$$

It is evident that the smaller c_2 in (11) the more will a in (12) approach unity ($a \leqslant 1$). c_2 increases with increasing CT-interaction in the ground state of the complex. Hence, the closer a is to unity, the smaller is this interaction.

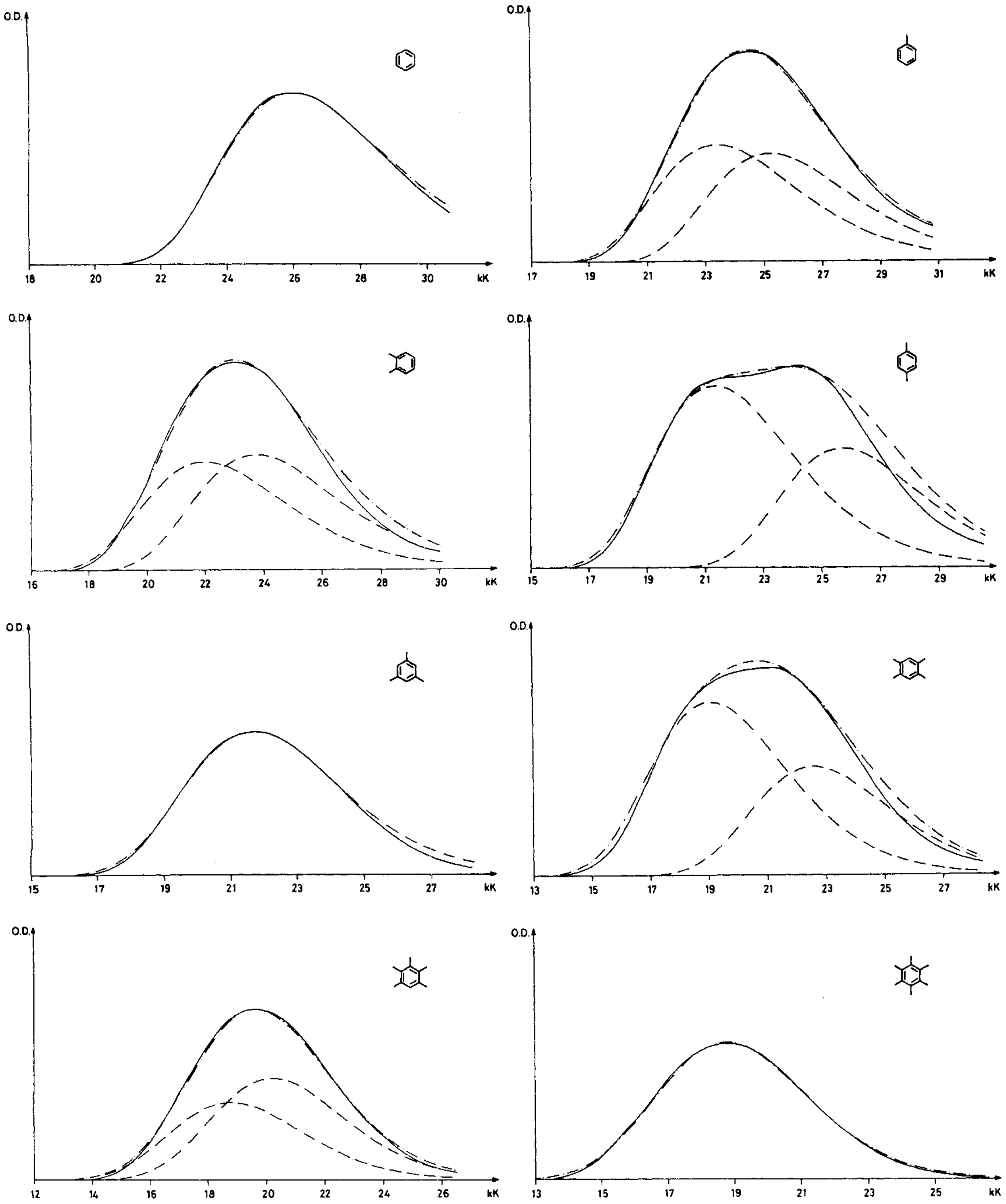

Fig. 1. *Deconvoluted CT-spectra in solution phase*

For the present complexes in solution phase we obtain (in eV)

$$a = 0.768 \pm 0.041, \; b = 3.812 \pm 0.353. \tag{13}$$

The correlation, which involves both $IP^1_v/h\nu^1_v$ and $IP^2_v/h\nu^2_v$ is shown in Fig. 2a; the good fit supports the deconvolution procedure used to determine the $\tilde{\nu}^i_v$-values listed in Tab. 5. It is interesting however to note the rather low a-value in (13), indicating at first sight a considerable CT-interaction in the ground state.

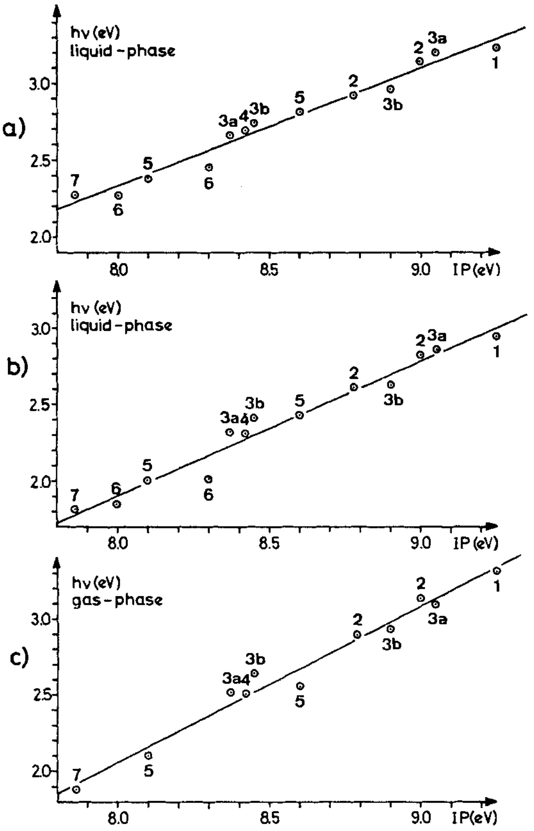

Fig. 2. *Correlation between IP_D and $h\nu^{CT}$* (see text)

A modification of (12) shows a way out of this problem. It has since long been recognized [15] and is supported *e.g.* by a recent high quality *ab-initio* calculation for benzene-carbonylcyanide [16] that the dispersion energy E_{disp} contributes significantly to the total binding energy. Since TCNE-contrary to the acceptor mentioned above – is non-polar, E_{disp} will be of even greater importance in the present series, for *Debye*-induction is absent. Consider the *London*-equation

$$E_{disp} = \frac{3\, IP_D\, IP_A}{2\,(IP_D + IP_A)} \cdot \frac{\alpha_D\, \alpha_A}{d^{\,6}_{AD}} \tag{14}$$

where $\alpha_{\mathbf{D}}$, $\alpha_{\mathbf{A}}$ are the polarizabilities of **D** and **A**, resp. For two related donors **D** and **D′** with same **A** and assuming equal $d_{\mathbf{AD}}$, the ratio R of the respective E_{disp}-contributions is

$$R = \frac{E_{\mathrm{disp}}(\mathbf{D'A})}{E_{\mathrm{disp}}(\mathbf{DA})} = \frac{IP_{\mathbf{D'}}\,(IP_{\mathbf{D}} + IP_{\mathbf{A}})}{IP_{\mathbf{D}}\,(IP_{\mathbf{D'}} + IP_{\mathbf{A}})} \cdot \frac{\alpha_{\mathbf{D'}}}{\alpha_{\mathbf{D}}} = r_{IP} \cdot r_{\alpha} \qquad (15)$$

For **D** = **1**, **D′** = **4** and **A** = TCNE[5]) we obtain from Tab. 4 $r_{IP} = 0.95$ and from [8] $r_{\alpha} = 1.56$, yielding R = 1.48. This is almost exactly equal to the ratio $\Delta H°$ (g) (**1A**) / $\Delta H°$ (g) (**4A**) = 1.5 obtained from Tab. 2. Hence, the 50% higher stability of **4A** with respect to **1A** can be directly related to the ratio of dispersion energies associated with these systems. Specifically we note that r_{α} is the decisive term furnishing this result. Hence, a < 1 in (13) may in fact indicate strong E_{disp}-variations in the series. If so, then a′ in (16)

$$h\nu_v^i - \Delta H_1^\circ = a'IP_v^i - b' \qquad (16)$$

should be nearer unity. We obtain from the data of Tab. 1 (in eV)

$$a' = 0.883 \pm 0.051, \; b' = 5.057 \pm 0.433, \qquad (17)$$

i.e. a significant increase of the slope (Fig. 2b). Clearly, a′ is still smaller than unity, but we believe that this is due to a solvation effect. This can be seen by inserting into (16) the appropriate gas phase values, listed in Tab. 2 and 4. This furnishes (*cf.* Fig. 2c):

$$a' = 1.019 \pm 0.055, \; b' = 6.096 \pm 0.473, \qquad (18)$$

i.e. a slope of unity, indicating negligible CT-interaction in the ground state of the complexes.

We finally point out that the good correlation of Fig. 2 supports the implicit assumption made in this work that the two resolved CT-absorptions arise from transitions involving two different **D**-MO's and one single **A**-MO.

The ground state conformational question. On the basis of Fig. 3 the following relationship for the free energy of dissociation ΔG^i for a complex **DA** in its i-th vertically produced CT-state into ionic fragments $\mathbf{D}^+$ (in electronic groundstate for i = 1, in electronic excited states for i > 1) and ground state $\mathbf{A}^-$ holds to a good approximation:

$$\Delta G^i = IP_v^i - EA - h\nu_v^i - \Delta G^\circ \qquad (19)$$

with:

IP_v^i = i-th vertical ionisation potential of donor[6]),
EA = electron affinity of acceptor,
$h\nu_v^i$ = i-th vertical CT-transition energy[6]),
ΔG° = free energy of formation of ground state **DA** with respect to separated **D** and **A**,
i = 1, 2 for the present systems.

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[5]) IP_v^1 (TCNE) = 11.79 eV, private communication from Prof. *H. Bock*, Frankfurt.

[6]) In principle the adiabatic values ought to be taken. Unfortunately these are not known for the present systems. From known adiabatic transition energies of fluorescent molecular complexes, the vertical-adiabatic energy difference is about equal to that usually found between IP_V and IP_a, leading to a near cancellation of errors in (19).

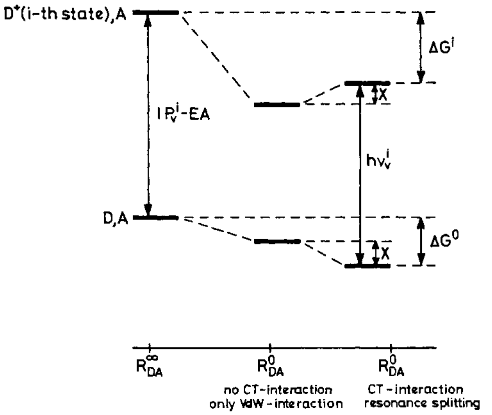


Fig. 3. *Free energy diagram for ground- and i-th CT-state of a* **DA** *complex*

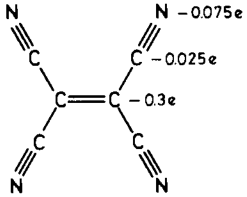
Tab. 6. *ΔG^i-terms* (eV) *for gas and solution phase* (see eqn. (11) and text). *Values based on EA = 2.77 eV for TCNE* [17]

TCNE-complex	gas phase		solution phase	
	$\Delta G^1(g)$	$\Delta G^2(g)$	$\Delta G^1(\ell)$	$\Delta G^2(\ell)$
1	2.99		3.25	
2	2.90	2.90	3.13	3.13
3a	2.88	2.97	3.00	3.14
3b	2.82	2.99	3.00	3.23
4	2.90		3.04	
5	2.95	3.07	2.99	3.11
6	---	---	3.07	3.20
7	2.97		2.86	

In Tab. 6, ΔG^1 and ΔG^2 are listed for the present complexes for both the gas and the solution phase. The ΔG^i(g)-values are representative for the *Coulombic* attraction C^i between **D**$^+$ (i-th state) and **A**$^-$ (*cf.* Fig. 3), since – as discussed earlier – resonance interaction between 'no-bond' and 'dative' configurations is small for the present systems (X small). It is remarkable to note that all C^1 are very similar in magnitude, their mean value and standard deviation being 2.94 ± 0.07 eV. This result implies at first sight that d_{DA} and the hole distribution in **D**$^+$ are the same for the whole series, in line with the inductive model for alkyl groups which is usually applied in PES. for the discussion of IP-changes induced by alkyl substitution.

From ESR. spectroscopy on radical cations of methylated benzenes, however, it is known that a significant charge migration of 20–25% onto methyl groups occurs [18], requiring a hyperconjugative model. If – as usually done – TCNE is approximated by a negative unit point charge located 3.5 Å above the centre of the benzene rings, this charge dispersion in **D**$^+$ should have a sizeable effect on their mutual attraction. This may be visualized for the two extremes **1**$^+$**A**$^-$ and **7**$^+$**A**$^-$ where the hole is symmetrically distributed in **D**$^+$. For **1**$^+$ every C-Atom carries $+{}^1/_6$ e. For **7**$^+$, assuming a charge dispersion of 25% onto the methyl groups, each C-atom of benzene carries $+ ^3/_4 \cdot ^1/_6$ e, each methyl group, approximated by a point charge centered at the C-atom $+ ^1/_4 \cdot ^1/_6$ e. Using standard bond lengths one finds $C(\mathbf{1}^+\mathbf{A}^-) = 3.82$ eV, $C(\mathbf{7}^+\mathbf{A}^-) = 3.47$ eV. Experimentally, however, both C-terms (*i.e.* ΔG^i) are about equal. The admission of a possible contamination of the ΔG^i-terms by some X-contribution due to CT-interaction does not resolve the discrepancy since $X(\mathbf{7A}) > X(\mathbf{1A})$ as indicated by $h\nu_V(\mathbf{7A}) < h\nu_V(\mathbf{1A})$ and $\Delta G°(\mathbf{7A}) > \Delta G°(\mathbf{1A})$, if the coupling parameter between no-bond and CT-configuration is about equal for both complexes.

A way out of this is found on departing from the point charge model of $TCNE^-$. From MINDO/3-calculations the following charge dispersion pattern is obtained



Accounting for this would clearly render the C-terms of the series more equal, though there are still $^6/_{10}$ of a negative charge confined to the central part of the anion. In addition, one could visualize a slight shortening of d_{DA} taking place with increasing number of methyl substituents. This is suggested by the strong increase in $\Delta H°(g)$ (Tab. 2) and would compensate for the increasing charge dispersion with increasing substitution.

A closer look at Tab. 6 reveals that for the gas phase substrates where two CT-transitions are resolved $\Delta G^1 < \Delta G^2$ is valid. (The same observation is made for the solution phase complexes to be discussed later.) As discussed above for weak complexes the main contribution to their total binding energy and therefore the dominant factor determining their overall structure is of classical electrostatic type. However, in line with *Mulliken*'s maximum overlap principle, final conformational preferences may well be traced back to maximum CT-interaction between no-bond and lowest dative configurations. If this were the case for the present complexes then ΔG^1 would be smaller than the value expected on purely electrostatic grounds. ΔG^2 however would not be effected since for such a conformation the higher excited 'dative' configuration is orthogonal to the 'no-bond' one. It can be shown numerically that the *Coulombic* interaction between TCNE with the above charge distribution and a positive charge distributed according to either of the real representations of the benzene e_{1g}-orbitals ($d_{DA} = 3.5$ Å) [9] are equal within 0.02 eV [11b]. Hence if the present substrates follow *Mulliken*'s principle, $\Delta G^1 < \Delta G^2$ is expected. This prediction is fulfilled in view of Tab. 6. These arguments imply that the present complexes exist predominantly in that conformation which leads to maximum overlap between the HOMO π^1 of **D** and the LUMO π^* of **A**, and that steric factors are of less importance. This conclusion conflicts with that proposed in [11a] where the intensity ratio for the two CT-bands was related to the concentration ratio of different conformers present in the complex equilibrium. The implicit assumptions made therein were that both transition moments M^1_{CT} for $h\nu^1_V$ and M^2_{CT} for $h\nu^2_V$ are monotonically increasing functions of overlap (S) between the MO's involved in the transition, satisfying the boundary conditions

$$\begin{aligned}&\text{(i)}\quad M^1_{CT}\,(S^1 = 0) = M^2_{CT}\,(S^2 = 0) = 0,\\ &\text{(ii)}\quad M^1_{CT}\,(S^1 = S^1_{max}) \approx M^2_{CT}\,(S^2 = S^2_{max}),\end{aligned} \tag{20}$$

where $S^1 = <\pi^1/\pi^*>$, $S^2 = <\pi^2/\pi^*>$

π^1: HOMO of **D**

π^2: next lower lying occupied MO of **D**

π^*: LUMO of **A**

Both assumptions are, however, weak. Concerning (i), it has been shown that appreciable intensity for a CT-transition may result from intensity borrowing [11b] [19]. More important, (ii) fails to show up in *p*-disubstituted benzene derivatives of the type investigated in [11c]. The conclusion to be drawn from this latter work is that hyperconjugation between the symmetric benzene π-orbital and appropriate substituent orbitals results in donor orbitals of rather different shape, associated naturally with other transition moments than benzene itself. The same is true for the present alkylbenzene donors since we have shown above from energetic considerations, that hyperconjugation is important in their ionic states. Hence, any direct relation between variations in the intensity ratio of the two CT-bands, and in the conformer equilibrium constant upon substitution is dangerous, since the intrinsic transition moments for each conformer change themselves in a non-easily predictable manner.

Concerning the ionic photodissociation of the solution complexes. Turning now to the $\Delta G^i(l)$-values we observe a close correspondence to those of the gas phase which is of practical value since solution measurements are easier to carry out. The latter may serve therefore to estimate gas phase free energies of dissociation of excited CT-complexes. This, however, is a purely empirical finding since the $\Delta G^i(l)$-values in no way truly represent this quantity, being calculated from (19) on the basis of gas phase values for IP and EA. The true values $\Delta G^i_t(l)$ which shall now be estimated for the smallest and the largest complex **1A** and **7A**, resp. are obtained from a thermodynamic cycle:

$$\begin{aligned}\Delta G^i_t(l) &= \Delta G^i(l) + [\Delta G^o_{solv}(\mathbf{D}^+) - \Delta G^o_{solv}(\mathbf{D})] + [\Delta G^o_{solv}(\mathbf{A}^-) - \Delta G^o_{solv}(\mathbf{A})]\\ &= \Delta G^i(l) + \Delta\Delta G^o_{solv}(\mathbf{D}^+/\mathbf{D}) + \Delta\Delta G^o_{solv}(\mathbf{A}^-/\mathbf{A}).\end{aligned} \tag{21}$$

The solvation terms in (21) can be obtained on the basis of known oxidation and reduction half wave potentials, $E^{1/2}_{ox}$ and $E^{1/2}_{red}$ resp.:

$$\Delta\Delta G^o_{solv}(\mathbf{D}^+/\mathbf{D}) = E^{1/2}_{ox} - \mathrm{IP} + 5.07\ \mathrm{eV} \tag{22a}$$

$$\Delta\Delta G^o_{solv}(\mathbf{A}^-/\mathbf{A}) = E^{1/2}_{red} + \mathrm{EA} - 5.07\ \mathrm{eV}, \tag{22b}$$

the numerical factor being associated with the reaction in the SCE-reference system (compare [20]). Taking EA(TCNE) = 2.77 eV [17], IP(**1**) = 9.25 eV [13], IP(**7**) =

7.86 eV [13], $E^{1/2}_{\text{ox}}$ (**1**) = 2.38 eV [21][7]), $E^{1/2}_{\text{ox}}$ (**7**) = 1.46 eV [21][7]) and $E^{1/2}_{\text{red}}$ (TCNE) = –0.24 eV [23][8]), we obtain

$$\begin{aligned} \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{1}^{+}/\mathbf{1}) &= -1.8 \ \text{eV} \\ \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{7}^{+}/\mathbf{7}) &= -1.33 \ \text{eV} \\ \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{A}^{-}/\mathbf{A}) &= -3.28 \ \text{eV} \end{aligned} \tag{23}$$

These values, valid for MeCN as solvent, shall be transformed into those appropriate to the present solvent CH_2Cl_2 using the *Born* equation [24] as a basis. Here, the implicit assumption is made that the change of solvent will predominantly affect $\Delta G^{\circ}_{\text{solv}}$ of the charged species. We derive

$$\Delta\Delta G^{\circ}_{\text{solv}}(CH_2Cl_2) = \Delta\Delta G^{\circ}_{\text{solv}}(\text{MeCN}) + \frac{e^2}{2r}\left(\frac{1}{\varepsilon_{GH_2Cl_2}} - \frac{1}{\varepsilon_{\text{MeCN}}}\right) . \tag{24}$$

With the dielectric constants $\varepsilon_{CH_2Cl_2} = 9.08$, $\varepsilon_{\text{MeCN}} = 37.5$ [8] and taking r = 3.5 Å we obtain

$$\begin{aligned} \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{1}^{+}/\mathbf{1}) &= -1.64 \ \text{eV} \\ \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{7}^{+}/\mathbf{7}) &= -1.17 \ \text{eV} \\ \Delta\Delta G^{\circ}_{\text{solv}}(\mathbf{A}^{-}/\mathbf{A}) &= -3.12 \ \text{eV} \end{aligned} \tag{25}$$

or with (19) and Tab. 6

$$\begin{aligned} \Delta G^{\text{i}}_{\text{t}}(l) &= -0.75 \ \text{eV for } \mathbf{1}^{+}\mathbf{A}^{-} \\ \Delta G^{\text{i}}_{\text{t}}(l) &= -0.59 \ \text{eV for } \mathbf{7}^{+}\mathbf{A}^{-} \end{aligned} \tag{26}$$

These values indicate that dissociation of the present excited CT-complexes into solvated ions is thermodynamically feasible in CH_2Cl_2-solution. Indeed, in [25] $TCNE^{-}$ has been observed as a transient species after flash photolysis of the benzene-TCNE complex in this solvent. On the other hand no photodissociation could be detected in an alkane matrix, where ionic solvation of course is much less effective. This can also be seen by inserting into (24) $\varepsilon = 2$ as average dielectric constant for aliphatic hydrocarbons, which leads to significantly positive $\Delta G^{\text{i}}_{\text{t}}(l)$-values in (26). In [26] it was found that the dissociation quantum yield for $\mathbf{7}^{+}\mathbf{A}^{-}$ is much smaller than that of $\mathbf{1}^{+}\mathbf{A}^{-}$ (**A** = TCNB). Since the electronic structure of the two excited complexes is presumably rather similar, this finding was explained on the basis of a greater intra-complex radiationless transition rate for $\mathbf{7}^{+}\mathbf{A}^{-}$. Eqn. (26) in conjunction with the *Bell-Evans-Polanyi* principle [27] indicates that the dissociation rate for $\mathbf{7}^{+}\mathbf{A}^{-}$ is smaller than that for $\mathbf{1}^{+}\mathbf{A}^{-}$. Hence, as an alternative explanation, the non-dissociative processes in $\mathbf{7}^{+}\mathbf{A}^{-}$, even if they would have an equal rate to those in $\mathbf{1}^{+}\mathbf{A}^{-}$, are more competing.

Photodissociations of EDA-complexes have rarely and only recently been studied [26] [28] [29]. It is noteworthy that in only one case has the free $\mathbf{D}^{+}$-species been identified (α-methylstyrene^{+} [29]). Several reasons may be responsible for this, among them the overlap of $\mathbf{D}^{+}$-bands with those of $\mathbf{A}^{-}$, the high reactivity of $\mathbf{D}^{+}$ *etc.*

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[7]) Values measured in acetonitrile and corrected for SCE-reference system (*cf.* [22]).

[8]) Value measured in acetonitrile *vs.* SCE-reference.

We are currently engaged in establishing optimal conditions for the observation of a great variety of donor ions. Their spectra may then be compared with the predictions from PE-spectroscopy. In order to render dissociation more competitive with respect to non-dissociative processes the influence of strong electric fields (second *Wien* effect [30]) shall be investigated.

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