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Molecular Complexes and Their Spectra. XX. Gas-Phase Electron Donor–Acceptor Complexes[1]

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Abstract: The electron donor–acceptor complexes of *p*-xylene, *o*-xylene, mesitylene, and durene with tetracyanoethylene (TCNE) and of dimethyl sulfide, diethyl sulfide, and tetrahydrothiophene with iodine have been studied spectrophotometrically in the gas phase over a temperature range of 90–150°. In all cases the charge-transfer absorption band is shifted to shorter wavelengths in the gas phase by amounts of 700–3000 cm^{-1}, and in the case of the TCNE complexes this shift is greater the fewer the number of methyl groups on the benzene ring. The extinction coefficient of the gas-phase charge-transfer absorption band is decreased by a factor of 3–20 from its corresponding solution value, while the equilibrium constant is increased by a factor of 3 or more. The blue-shifted iodine visible absorption band found in the solution spectra of the sulfide complexes with iodine is observed in the gas phase with an intensity decrease of at least a factor of 10 from its solution value. Finally, the heats of formation of the TCNE complexes are approximately twice as great in the gas phase as in solution while the heats of formation of the iodine complexes are approximately equal in the two phases. Suggestions are made to explain the differences and similarities of the properties of these complexes in the two phases.

Electron donor–acceptor (EDA) molecular complexes are associations of two or more molecules in their ground electronic states. The stoichiometry of these complexes in solution is almost exclusively 1:1, and the energy required to dissociate such a complex into its two component molecules is somewhat greater than typical van der Waals energies, but less than usual chemical bond energies. Solutions of these complexes usually have intense absorption spectra which are not characteristic of either component separately.

At present there is a large amount of data on these EDA complexes in solution and, to a lesser degree, in the solid state. The theoretical description of these complexes provided by Mulliken[2] applies strictly, however, only to the gas phase at low pressures. In solutions and in solids, the density of molecules is sufficiently high that the state of the complex can no longer be considered to result uniquely from the interaction between a single donor and a single acceptor molecule. In view of the "soft" or weak nature of the charge-transfer (CT) bond as compared with usual chemical bonds and the large difference in polarity of the ground and excited (CT) states, it is to be expected that the presence of solvent or of nearby EDA complex molecules will markedly alter the properties of the isolated complex. In solutions it is necessary to consider the effect of solution nonideality on the evaluation of equilibrium constants and extinction coefficients (ϵ). In solids it is necessary to consider the interaction of a complex with neighboring complex molecules, which in some cases can lead to the formation of an $\infty:\infty$ complex instead of distinct 1:1 complexes. In both solutions and solids it is necessary to consider the effect on

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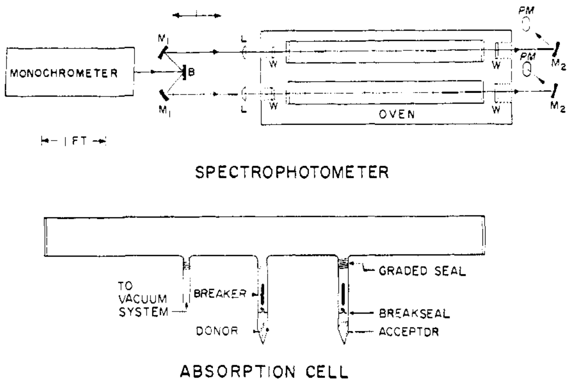
[1] (a) This work provided the basis for a thesis submitted to the Department of Chemistry, The University of Chicago, in partial fulfillment for the Degree of Doctor of Philosophy. (b) The research reported was supported by the Office of Naval Research, Physics Branch, under Contract Nonr-2121 (01), and later under Contract N00014-67-A-0285-0001. (c) The original data of this article will appear in a forthcoming issue of the Technical Report of the Laboratory of Molecular Structure and Spectra.

[2] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).



SPECTROPHOTOMETER

ABSORPTION CELL

Figure 1. Experimental apparatus. In the diagram of the spectrophotometer, lenses L, windows W, mirrors M_2, and the oven were added to the original spectrophotometer.

the complex of placing it in a medium whose dielectric constant is appreciably greater than unity. The effects of these complications can be greatly reduced by studying EDA complexes in the gas phase.

Recently there have been several reports of studies of gas-phase EDA complexes.[3-6] In the present paper, the results of an extension of previous work on gas-phase complexes of tetracyanoethylene (TCNE) are presented together with some results obtained on iodine complexes.

Experimental Section

The spectrophotometric measurements reported in the present paper were obtained using a Warren "Spectracord," a double-beam spectrophotometer, modified for use with absorption cells 100 cm in length. These absorption cells were contained within an oven which was operated over a temperature range of 90–150°. The temperature of the oven was regulated by a proportionally controlled thermoregulator to ±0.5°. In the diagram of this equipment (see Figure 1), the parts labeled M_1,B, and PM are parts of the original spectrophotometer. In the modified section, all transmission optics (L, W) are of fused quartz, and the mirrors (M_2) are constructed by evaporating aluminum films onto glass surfaces.

Absorption cells were initially constructed by sealing[7] quartz windows to Pyrex tubes using silver chloride as a cement after platinizing both surfaces. This technique was adequate for the experiments with TCNE, but the organic sulfides appeared to react with the silver chloride and it could not be used with them. Furthermore, sealing windows to tubes using silver chloride is a time-consuming process, and the resulting seals are somewhat fragile. As a result, they were used only for the system TCNE + *p*-xylene. Absorption cells (see Figure 1) for use in visible light were constructed in the university glass shop by sealing Pyrex disks (2 in. × $^1/_{16}$ in.) to Pyrex tubes. Absorption cells for use with ultraviolet light were constructed by sealing fused quartz disks (2 in. × $^1/_{16}$ in.) to Vycor tubing. Three leadout tubes from the cells were necessary to fill and evacuate the cells. The use of Vycor tubes necessitated the use of Vycor-to-Pyrex graded seals on these leadout tubes.

Construction of cells in the above manner permitted the use of entirely grease-free systems. This was accomplished by sealing known quantities of the donor and acceptor molecules into separate break-seals, attaching these to an absorption cell, and breaking the seals as required. The amount of donor or acceptor in the break-seals was determined in the following manner. The crystalline acceptors studied herein, either TCNE or I_2, were placed in tared break-seals (8-mm o.d.) and weighed by difference on a semimicro balance. The weight of acceptor used was 8–20 mg. The crystals in the break-seal were then cooled; the break-seal was connected by means of rubber tubing to a vacuum system, evacuated, and sealed under vacuum. Volatile hydrocarbons were placed in tared break-seals (10-mm o.d.) by pipetting in the approximate amount desired. The break-seal was then sealed as in the case of the acceptor break-seal, and after cooling both pieces of the break-seal were weighed and the amount of donor was determined by difference. A buoyancy correction for the change in the volume of air displaced by the break-seal after sealing, amounting to 2–4 mg, was necessary. This was at most a 4% correction since the weight of the donor was usually in the range of 100–1000 mg.

The volume of the cells (~1.7 l.) was determined with an accuracy of better than 1% by weighing the cells empty and filled with distilled water, the volume being calculated from the weight of water and its density at the filling temperature. The concentration of donor was thereby known with an accuracy of 1% or better, and the concentration of acceptor with an accuracy of 2%. The volume of the cells was calculated to change by less than 0.2% over the temperature range used. The relative error inherent in all absorbance measurements ranges from ~5 to 2% in the absorbance range (0.1 to 1.0) used in the investigation. A simple error analysis of the equations used to analyze the data of these experiments indicates that, for the values used in this experiment, the above error estimates an uncertainty in the ordinate very nearly equal to the value of the standard deviation calculated by a least-squares fit of the data. This indicates that the above error estimates are reasonable.

To record spectra, break-seals filled in the above manner were sealed to an absorption cell. The cells were then attached to the vacuum system and evacuated with light flaming of the cell. When the pressure was in the range 10–100 μ, the cell was sealed under vacuum and placed in the oven. This was usually done the evening preceding the day the measurements were taken. The "zero" absorbance base line on the spectrophotometer was then adjusted until several steady base lines were recorded. The oven was opened, and the break-seal containing the least volatile component was broken and lightly flamed to assure that all material was in the main body of the absorption cell. In the experiments described here, TCNE showed no absorption in the region examined while I_2 had a small, but significant, absorbance (0.04 at the maximum). Therefore, the base line with I_2 vapor alone in the cell was recorded to make correction at a later time possible. Finally the break-seal containing the donor was broken and the temperature increased to ~150°. After 1 hr at 150°, the spectra showed no change with time and the temperature was lowered in steps of ~7°, recording the absorption spectrum at least twice at each temperature.

For each of the complexes for which thermodynamic data are reported, spectra were recorded at 8 to 13 temperatures for mixtures of seven to ten different concentrations. Each concentration requires filling a cell in the above manner and recording the absorption spectra at 8 to 13 temperatures. While each spectrum was being recorded, the readings of five thermocouples in contact with the absorption cell were recorded and averaged. The average deviations of these readings indicated that the temperature could be reproduced on successive days to within ±0.5°.

The hydrocarbons (Eastman Organic or Aldrich) used in these experiments were the purest grade obtainable, although not zone refined, and were further purified by conventional methods. Usually only the middle third fraction of a slow distillation was used in experiments. The iodine (Baker) and TCNE (Eastman Organic) were sublimed twice under vacuum at vapor pressures of 1–10 mm prior to use. The organic sulfides (Aldrich) used were washed successively with 5% aqueous H_2SO_4, 5% aqueous NaOH, and distilled water. After drying with anhydrous $CaSO_4$, they were slowly distilled. All boiling points agreed well with accepted literature values.

The solvents used in the solution work were either spectral grade or specially purified. Purification of *n*-perfluoroheptane, C_7F_{16}, was attempted, although in no case could results as good as those reported[8,9] in the literature be obtained. Passage of 1 l. of C_7F_{16}, refluxed 48 hr with cleaning solution, through a 3-ft silica gel column would give, however, 10 to 15 ml of material which showed no absorption in a 1-cm cell down to 205 mμ. For most of the work, slightly impure perfluoroheptane (absorbance 0.2 at 220 mμ) was used. The solution spectra were recorded at 25° on a Beckman DK-2 spectrophotometer.

Treatment of Data

In order to remove some of the arbitrariness and difficulty in accurately assessing the error in a graphical

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[3] (a) F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965); (b) M. Kroll and M. L. Ginter, *J. Phys. Chem.*, **69**, 3671 (1965).

[4] J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

[5] J. Prochorow, *ibid.*, **43**, 3394 (1965).

[6] J. Prochorow and A. Tramer, *ibid.*, **44**, 4545 (1966).

[7] S. W. Benson, *Rev. Sci. Instr.*, **13**, 267 (1942).

[8] D. N. Glew and L. W. Reeves, *J. Phys. Chem.*, **60**, 615 (1956).

[9] D. Grafstein, *Anal. Chem.*, **26**, 523 (1954).

determination of the equilibrium constant K, and the extinction coefficient ϵ, the data obtained here were treated entirely by numerical procedures employing a computer program. These data were fitted by a least-squares calculation to (1) the Benesi–Hildebrand equation[10] and (2) the Scott equation.[11]

$$\frac{[\mathrm{A}]l}{a} = \frac{1}{K\epsilon}\frac{1}{[\mathrm{D}]} + \frac{1}{\epsilon} \qquad (1)$$

$$\frac{[\mathrm{A}][\mathrm{D}]l}{a} = \frac{1}{\epsilon}[\mathrm{D}] + \frac{1}{K\epsilon} \qquad (2)$$

where [A] and [D] represent the initial concentrations of acceptor and donor respectively, l represents the path length of the light in the absorption cell, and a represents the absorbance. Both equations, 1 and 2, were derived by assuming that $[\mathrm{D}] >> [\mathrm{A}]$. If no assumption regarding the relative concentrations of D and A are made, then one obtains the equation

$$\frac{1}{K} = \frac{[\mathrm{D}][\mathrm{A}]l\epsilon}{a} - \{[\mathrm{A}] + [\mathrm{D}]\} + \frac{a}{\epsilon l} \qquad (3)$$

which contains two unknowns, K and ϵ, which, at a given temperature and wavelength, are the same for all concentrations of A and D. Equation 3 can, therefore, be solved by taking all possible distinct pairs of combinations of data at a given concentration (*i.e.*, $[D_i]$, $[\mathrm{A}_i]$, a_i) and solving the simultaneous equations for K and ϵ, and then averaging these results.

Equations 1 and 2 gave results in good agreement with each other; neither yielded results consistently different from the other. Equation 3 gave results which usually agreed with those obtained using eq 1 and 2 but was sometimes, particularly at higher temperatures, in poor agreement with them. The poor agreement is due to the sensitivity of the roots of eq 3 to random errors in [A], [D], and a. This point has been discussed by Johnson and coworkers.[12] The results presented in this work are the average values obtained using eq 1 and 2.

The usual method for determining the energy of formation, ΔE, of the complex is to plot ln K_c *vs.* T^{-1}. The slope of this straight line is equal to $-\Delta E/R$. If ϵ is independent of temperature, then plotting ln $(K_c\epsilon)$ *vs.* T^{-1} gives a straight line with a slope equal to $-\Delta E/R$ but with a different intercept. (Actually ϵ should have a slight temperature dependence, but this should not appreciably affect the values obtained for ΔE). The value for ΔE was calculated using this latter method because the precision of $K_c\epsilon$ is greater than the precision of K_c alone.

Results

Frequently, it happens that the CT absorption band of the EDA complex occurs near an absorption band of either the donor or the acceptor molecule. The CT absorption band in the gas phase occurs at higher frequencies (1000–3000 cm^{-1}) than in solution. Since the gas phase to solution shift of the spectrum of the donor or acceptor molecules alone is usually much lower than this value, the spectral shift on going to the gas phase may cause the CT absorption spectrum to be superimposed on the absorption spectrum of one of the components. Such a superposition of spectra makes the analysis of data less precise than would otherwise be the case. The systems studied in the present work are very favorable with respect to this difficulty. The CT absorption spectra of the TCNE complexes occur in the visible region of the spectrum, far removed from the spectra of the component molecules; and the CT absorption spectra of the I_2 complexes occur in the near-uv region where ($\lambda > 270$ mμ) the extinction coefficients of the organic sulfides are less than unity.

In order to use iodine as an acceptor, it was necessary to examine the behavior of the spectrum of I_2 vapor in the region 250–300 mμ. The absorbance of I_2 solutions in organic solvents in this region has been reported[13,14] to increase more rapidly than the iodine concentration. It has been shown[13] that this is caused by the formation of an I_2–I_2 complex which also absorbs in this region. It has been suggested that this may be an EDA complex.[15] Similar behavior has been found for bromine vapor;[16] and high-temperature studies of iodine vapor,[17] using photographic methods, indicated some deviations from a linear dependence on vapor concentration. To the limit of accuracy of the present work, however, the absorbance of I_2 vapor is a linear function of concentration in the low concentration range (0.5 to 5×10^{-4} *M*) used here. Furthermore, the variation of the shape of the absorption curve and the maximum as a function of temperature are in excellent agreement with the predictions of Sulzer and Wieland,[18] whose model was formulated to explain the temperature dependence of the continuous absorption spectra of halogens. It has been assumed, therefore, that the absorption spectrum of iodine vapor in this region is due solely to the molecule I_2 which has $\epsilon_{\max}$ 17 ± 1 at 268 mμ and 110°. Both uv and visible absorption spectra of I_2, as here observed, are in excellent agreement with those published by Rees[19] and seem to support his assumption that the uv absorption at these low pressures is due only to the I_2 molecule.

Charge-transfer absorption spectra were observed for gas-phase mixtures of TCNE with benzene toluene, *o*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene, and for gas-phase mixtures of dimethyl sulfide, diethyl sulfide, and tetrahydrothiophene with I_2. The wavelength of the maximum absorption and the half-width of the absorption band, as here observed, are listed in Tables I and II. No CT spectra were found for gas-phase mixtures of ethylene and TCNE. No CT spectrum was found for a gas-phase mixture of butadiene and TCNE immediately on mixing. After several hours at ~120°, an absorption spectrum appeared in the visible region. This spectrum did not change with temperature and, on cooling, thin films and crystals, not resembling TCNE, were found. This was taken to be evidence of polymerization and reaction.

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(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(11) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

(12) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964).

(13) P. A. D. DeMaine, *J. Chem. Phys.*, **24**, 1091 (1956).

(14) R. M. Keefer and T. L. Allen, *ibid.*, **25**, 1059 (1956).

(15) H. McConnell, *ibid.*, **22**, 760 (1954).

(16) E. A. Ogryzlo and B. C. Sanctuary, *J. Phys. Chem.*, **69**, 4422 (1965).

(17) G. Kortum and G. Friedheim, *Z. Naturforsch.*, **2a**, 20 (1947).

(18) P. Sulzer and K. Wieland, *Helv. Phys. Acta*, **25**, 653 (1952).

(19) L. Matheson and A. L. G. Rees, *J. Chem. Phys.*, **25**, 753 (1956).

Table I. Spectroscopic Constants of the CT Spectra of TCNE–EDA Complexes

Donor	ν_{max}, cm^{-1} ± 150 cm^{-1} Gas phase	n-Heptane	Red shift (cm^{-1}) on going to soln	Half-width, cm^{-1} Gas phase	n-Heptane
Benzene	29,590	26,530	3060		
Toluene	27,030	25,000	2030		
o-Xylene	25,380	23,870	1510	6100	6000
p-Xylene	23,530 26,880	21,880 25,100	1650 1780		
1,2,3-Trimethylbenzene	23,590	22,370	1220	5700	5400
Mesitylene	23,640	22,370	1270	5800	5600
Durene	21,140 23,260	20,000 22,000	1140 1260		
Pentamethylbenzene	20,960	20,000	960	5900	5900
Hexamethylbenzene	19,690	18,940	750	5300	5200

Table II. Spectroscopic Constants of the CT Spectra of Iodine–EDA Complexes

Donor	ν_{max}, cm^{-1} ± 150 cm^{-1} Gas phase	n-Heptane	Red shift (cm^{-1}) on going to soln	Half-width, cm^{-1} Gas phase	n-Heptane
Dimethyl sulfide	34,970	33,480	1490	5600	5300
Diethyl sulfide	34,480	33,000	1480	5800	5400
Tetrahydrothiophene	34,130	32,730	1400	5600	5400

No distinct CT maximum was found for gas-phase mixtures of I_2 and benzene; however, a mixture of mesitylene and I_2 vapor gave evidence of a CT absorption maximum[20] at ~305 mμ as compared with a value of ~330 mμ in hydrocarbon solvents. (This represents a blue shift of ~2500 cm^{-1} on going to the gas phase.) A gas-phase mixture of H_2S and I_2 had an absorption band (~300 mμ), which was not constant with time, and a mixture of I_2 and di-t-butyl sulfide produced a shoulder of high intensity on the long-wavelength side of the spectrum of di-t-butyl sulfide.

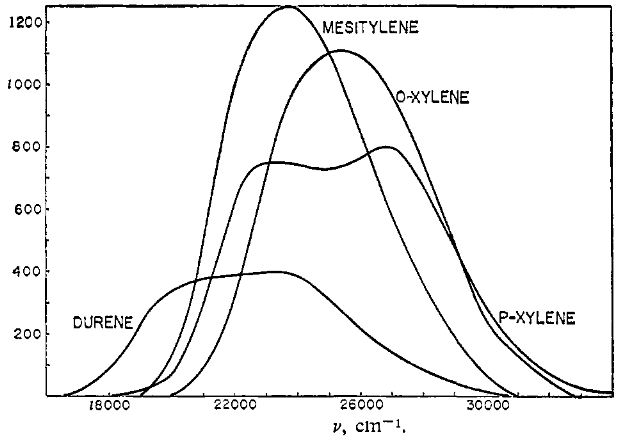

Figure 2. CT absorption spectra of gas-phase TCNE–EDA complexes. The units of ε are cm moles l.$^{-1}$.

The CT absorption spectra of p-xylene, o-xylene, mesitylene, and durene with TCNE, and of dimethyl sulfide, diethyl sulfide, and tetrahydrothiophene with I_2, were studied as a function of the concentration of donor and acceptor and of the temperature. After treatment by eq 1–3, the spectra shown in Figures 2 and 3 and the data in Tables III and IV were obtained. The errors listed for the various quantities in these tables are not the errors of any single determination but are approximately the average deviation of the values obtained. These errors are, in general, larger than the error of any given determination. The most precise quantity obtained in these experiments is the value of the product $K\epsilon$. This has been determined with a standard deviation of 2–5%. The individual values for K and ϵ are known with a precision of only 15–60% within 95% confidence limits. Usually the value of ϵ was determined from the average of the values of the four lowest temperatures, and then K was determined using this value and the value of $K\epsilon$ at some temperature. The oscillator strengths were evaluated by plotting graphs of the absorption curves using ϵ as the ordinate and ν as the abscissa. The area under this curve, which is equal to $\int \epsilon_\nu d\nu$, was measured with a planimeter. This introduces negligible errors into the determination of f, and so the fractional errors of f and ϵ are considered equal. Solution data, when available, are presented simultaneously with the gas-phase data and, in one case, the gas-phase results of other workers[4,21] are included.

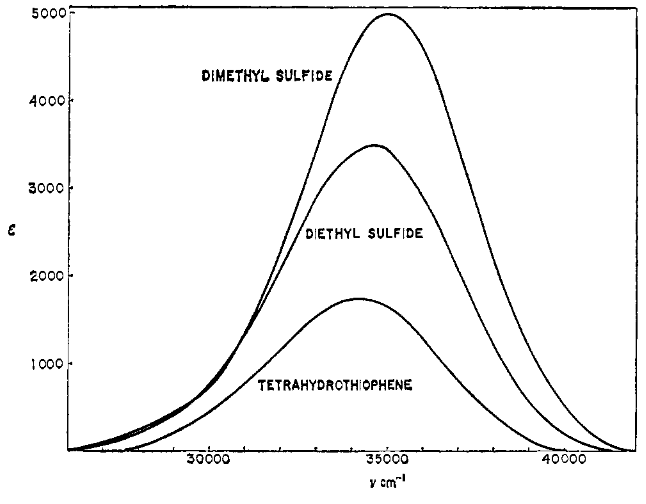

Figure 3. CT absorption spectra of gas phase iodine–EDA complexes. The units of ε are cm moles l.$^{-1}$.

The reason for the difference in the gas-phase values of K and ϵ obtained in this experiment and those of

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(20) This is in good agreement with the findings of other workers; private communication from M. Tamres.

(21) M. Tamres and J. M. Goodenow, *J. Phys. Chem.*, 71, 1982, (1967).

Table III. Thermodynamic and Spectroscopic Constants of the TCNE–EDA Complexes from CT Absorption Band

	p-Xylene		*o*-Xylene		Mesitylene		Durene	
	Gas[a]	Soln[b]	Gas[a]	Soln[b]	Gas[a]	Soln[b]	Gas[a]	Soln[b]
ϵ_{max}, l. mole^{-1} cm^{-1}	800 ± 250 (372 mμ)	2770	1100 ± 350	3860	1250 ± 375	3120	400 ± 150 (430 mμ)	2075
K_c (298°K), l. mole^{-1}	280 ± 100	7.20	350 ± 120	...	1020 ± 350	16.0	11800 ± 5900	49.5
K_c (373°K), l. mole^{-1}	23.1 ± 6.2	...	23.6 ± 6.4	...	45.8 ± 12.4	...	348 ± 120	...
$K_c\epsilon$ (373°K), l^2 mol^{-2} cm^{-1} [c]	18480 ± 1700	...	25960 ± 1850	...	57,250± 3550	...	153,600 ± 10000	...
ΔE, kcal mole^{-1}	−7.4 ± 0.5	−3.37	−8.0 ± 0.5	...	−9.2 ± 0.5	−4.52	−10.1 ± 0.8	−5.07
ΔH (373°K), kcal mole^{-1}	−8.1 ± 0.5	−3.37	−8.7 ± 0.5	...	−9.9 ± 0.5	−4.52	−10.8 ± 0.8	−5.07
ΔS, cal mole^{-1} deg^{-1}	−15.5 ± 2.0	−7.38	−17.0 ± 2.0	...	−18.7 ± 2.0	−9.61	−17.3 ± 3.1	−9.23
f (oscillator strength)	0.027 ± 0.008	0.097	0.029 ± 0.009	0.11	0.031 ± 0.009	0.075	0.013 ± 0.005	0.076

[a] Calculations based on standard-state concentration of 1 *M*. [b] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). [c] Error estimated with 95% confidence limits.

Table IV. Thermodynamic and Spectroscopic Constants of the Iodine–EDA Complexes from CT Absorption Band

	Dimethyl sulfide	Diethyl sulfide			Tetrahydrothiophene	
	Gas phase[a] (this work)	Gas phase[a] (this work)	Gas phase[a,b]	*n*-Heptane[a,c]	Gas phase[a] (this work)	*n*-Heptane[a,c]
ϵ_{max}, l. mole^{-1} cm^{-1}	5000 ± 2500	3500 ± 1000	11200 ± 1900	26400	1750 ± 400	27,000
K_c (298°K), l. mole^{-1}	220 ± 140	750 ± 250	226	200	2400 ± 400	252 ± 5
K_c (373°K), l. mole^{-1}	23 ± 12	58 ± 20	16.5	9.4	151 ± 35	17.8
$K_c\epsilon$ (373°K), l.^{2} mole^{-2} cm^{-1} [d]	115,000 ± 1150	203,000 ± 22900	184,800 ± 9200	248,160	264,250 ± 38,000	480,600
ΔE, kcal mole^{-1}	−6.7 ± 0.5	−7.6 ± 0.5	−7.7 ± 0.4	−8.9 ± 0.6	−8.3 ± 0.5	−7.8
ΔH (373°K), kcal mole^{-1}	−7.4 ± 0.5	−8.3 ± 0.5	−8.4 ± 0.4	−8.9 ± 0.6	−9.0 ± 0.5	−7.8
ΔS, cal mole^{-1} deg^{-1}	−13.6 ± 2.4	−14.2 ± 1.9	−15.0 ± 1.1	−19.4 ± 2.0	−14.2 ± 1.6	−15.0
f (oscillator strength)	0.13 ± 0.07	0.09 ± 0.03	0.28	0.6	0.04 ± 0.01	0.6

[a] Calculations based on standard state concentration of 1 *M*. [b] Reference 4. [c] Reference 23. [d] Error (of this work) estimated with 95% confidence limits.

Goodenow and Tamres[4,21] (G–T) is not understood. The values of the product $(K\epsilon)_{373°K}$ (see columns 2 and 3 of Table IV) are equal within the experimental error. The error occurs, therefore, in the separation of K and ϵ. It can be shown that, in a least-squares fit of data to the equation $y = mx + b$, changing y to $y' = ky$ preserves the ratio of m/b; similarly, changing x to $x' = cx$ preserves the value of b. Applying this to eq 1 one sees that a systematic error in the determination of either [A] or [D] (*e.g.*, if $[D] = 0.9[D]_{actual}$) cannot change K or ϵ, respectively. Since neither value agrees with those of G–T, the existence of a single systematic error can be ruled out. The possibility of systematic errors in the determination of both [A] and [D], however, still exists and may provide an explanation of the difference.

The energy of the CT transition is given by the equation[22]

$$h\nu_{CT} \cong I_D - E_A - e^2/R + X_1 - X_0 \qquad (4)$$

where I_D and E_A refer to the ionization potential of the donor and the electron affinity of the acceptor, respectively, in the configuration they have in the complex. The term $-e^2/R$ represents the coulombic attraction of the ions in the CT state where R is a measure of the separation of the charges on the ions. The terms X_0 and X_1 represent the resonance energy of interaction between the dative and no-bond states for the ground-state and charge-transfer states of the complex. In weak complexes this last term, $X_1 - X_0$, can be approximated as

$$X_1 - X_0 \cong \frac{C_2}{I_D - E_A - (e^2/R)}$$

where C_2 is approximately constant for a series of similar donors with a single given acceptor. (For a discussion of this approximation, see ref 22.) Furthermore, if the value of R is approximately constant for a series of donors with an acceptor, eq 4 can be written as

$$h\nu_{CT} \cong I_D - C_1 + \frac{C_2}{I_D - C_1} \qquad (5)$$

The constants C_1 and C_2 for the series of EDA complexes of methylated benzenes with TCNE are presented in Table V. One point which should be made here is that the value of I_D used here, and by others, is the gas-phase, and not the solution, ionization potential. Therefore, eq 5 has the further qualification that it is valid only if the ionization potential in solution $I_D{}^S$ is related to the gas-phase ionization potential $I_D{}^G$ as $I_{Di}{}^S = kI_{Di}{}^G$ for a series of donors $D_1, D_2, \ldots, D_n$.

Table V. ν_{max} of CT the Absorption Band as a Function of the Donor Ionization Potential for TCNE–Methylated Benzene–EDA Complexes

Solvent	C_1, eV[a]	C_2, eV^2 [a]	Std dev, eV
Gas phase	5.83	0.931	0.058
Perfluoroheptane	6.14	1.250	0.069
n-Heptane	6.27	1.296	0.065
Carbon tetrachloride	6.35	1.243	0.073

[a] See eq 5.

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(22) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

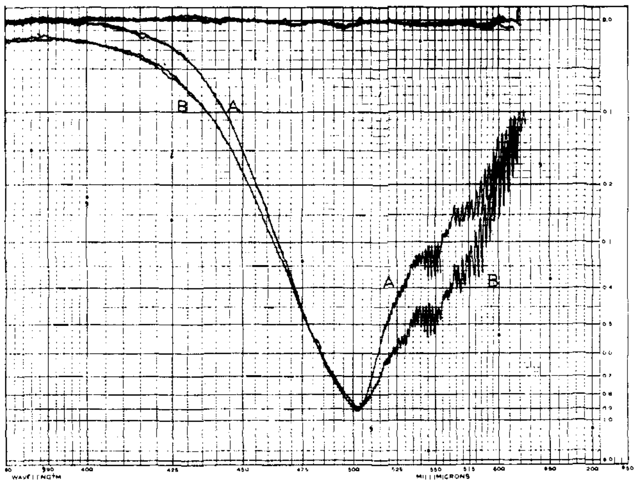

Figure 4. The effect of complexation on the visible absorption spectrum of iodine vapor. A is the absorption spectrum of 1.64 $\times 10^{-5}$ mole l.$^{-1}$ of I_2. B is the spectrum of 1.64 $\times 10^{-5}$ mole l.$^{-1}$ of I_2 + 1.63 $\times 10^{-3}$ mole l.$^{-1}$ of tetrahydrothiophene; both spectra were recorded at 98°. The vertical units are absorbance units. The heavy line at the top of the figure is the base line.

Finally, the effect of complex formation on the visible absorption spectrum of I_2 vapor was examined. Two effects are expected in this case: (1) a redistribution of, and a general increase in, the intensity of the absorption on the long-wavelength side of the maximum, and (2) the appearance of a blue-shifted absorption band characteristic of complexed I_2 molecules. The redistribution of, and general increase in, intensity on the long-wavelength side of the maximum is found when ~1 atm of any foreign gas is admitted to an absorption cell containing low pressures (1–5 mm) of I_2 vapor. This redistribution of intensity is interpreted as being due to line broadening on admission of foreign gas, which removes the false intensities obtained when there is nearly 100% absorption at line centers. The appearance of a blue-shifted absorption band, with ν_{max} shifted 3000–8000 cm^{-1}, is characteristic of strong EDA complexes, particularly n–σ complexes such as sulfide, ether, and amine complexes with I_2. The ϵ_{max} calculated for this shifted band varies somewhat but is usually larger than ϵ_{max} of I_2 in the solvent alone, the more so the stronger the complex.

The donors examined in the present work were the three organic sulfides in Table II, mesitylene and diethyl ether. No blue-shifted iodine band was definitely observed in any of these cases. In the most favorable case for observation of a blue-shifted band, that of tetrahydrothiophene (THT)-I_2 at 98°, about 25% of the iodine was complexed. If the value of ϵ_{max} for the blue-shifted band is about twice the value of ϵ_{max} for I_2 (Tamres and Searles[23] found a value of ϵ_{max} ~2000 for the blue-shifted band of I_2 complexed with THT at 438 mμ as compared with ϵ_{max} ~900 for unshifted iodine at 520 mμ), one expects, under the above conditions, to observe a blue-shifted band with about one-half the *absorbance* of the original unshifted maximum *absorbance*. At the same time the intensity of the unshifted I_2 absorption should decrease. Experimentally (see Figure 4), however, nothing but a slight increase in absorbance, extending from ~480 mμ to the onset of the CT absorption at about 350 mμ, constant (within experimental error) and equal to about 3% of the unshifted maximum is found. This is accompanied by a very slight decrease in the maximum absorption of the unshifted band. Even if the value of K is overestimated by a factor of 4 (the factor by which the values of $K_{373°K}$ differ between this work and that of G–T, Table IV), one still expects 6% of the iodine to be complexed, with a blue-shifted absorbance of about 12% of the maximum absorbance of the unshifted band. It is concluded from the data of this experiment that the ratio of ϵ_{max}(blue-shifted)/ϵ_{max}(unshifted) is decreased from a value of ~2 in solution to a value not greater than 0.2 in the gas phase for the THT–I_2–EDA complex. Possible reasons for this intensity decrease will be discussed below.

Discussion

The observed differences between the gas phase and the solution properties of EDA complexes which require discussion are: (1) the large red shift of the absorption maximum of the CT band on going from the gas phase to solution and its decrease with increasing methyl substitution for the series of TCNE complexes in Table I, (2) the differences between the heats of formation of the complexes in the two phases, and (3) the difference in the intensity of the CT absorption in the two phases and the lack, or large decrease in the intensity, of a blue-shifted absorption band in the visible spectrum of gas-phase EDA complexes of iodine.

Of these observed differences, the first is most definitely established since a red shift has been reported in all cases reported to date,[2–6] and the decrease in the red shift (listed in Table I) is well outside experimental uncertainties. The difference between the gas-phase and the solution values for ($-\Delta H$), however, apparently depends on the type of complex (*e.g.*, n–σ, n–π, or π–π) and is not a general property of all EDA complexes. The intensity decrease in the CT absorption band and the lack of the expected blue-shifted iodine band in the gas phase have been reported by all observers; however, the nonideality of solutions which is not taken into account by eq 1–3 prevents an accurate evaluation of the "true" thermodynamic K and, therefore, a true ϵ. Hence it is uncertain to what degree the observed differences between the gas-phase and the solution values of ϵ are indicative of real differences in the extinction coefficient of the CT absorption band between the two phases.

Prochorow and Tramer[6] (P–T) attempted to explain the large observed shift to longer wavelengths on going from gas to solution as being caused jointly by a dielectric shift and a cage effect of comparable magnitudes. The reason for attributing such a large red shift (averaging about 2500 cm^{-1} in their data) to a cage effect was based on a consideration of the potential curves of an EDA complex. In the neighborhood of R_e'' (see Figure 5a), the second derivative ($\partial^2 V/\partial R^2$) of the ground-state potential curve is small. (Henceforth R_e'' will refer to the equilibrium separation of the donor and acceptor molecules in the ground state and R_e' to their separation in the excited state.) Therefore, the force constant ($k = \partial^2 V/\partial R^2$) for a vibration of the complex along the intermolecular axis is very small, and the complex should be very susceptible to compression forces along this axis. This susceptibility to compression forces was

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(23) M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

predicted early in the development of the theory and has since been demonstrated by high-pressure studies of solution[24,25] and solid-state[26,27] CT spectra of EDA complexes. Prochorow and Tramer[6] state (p 4548), "the dissolved CT complex occupies a site in the quasicrystalline nature of the liquid and, if the dimensions of the solvent are not identical, the intermolecular forces will tend to decrease the volume occupied by the dissolved species, *i.e.*, to diminish the intermolecular distance in the complex (cage effect)." Assuming a coulombic attractive potential for the upper (CT) state, they estimate a slope of $\sim$10 cm^{-1}/m Å for the CT-state potential curve in the region of the ground-state equilibrium separation. Therefore, a decrease in the intermolecular separation of 0.1–0.2 Å is sufficient to account for the large red shift as caused by the cage effect. This model has been further developed by Trotter.[28] In addition to providing an explanation for the observed spectral shifts, this model also predicts that the overlap integral S (see ref 22) should increase because of the decreased intermolecular separation. The results of the increase in the overlap integral will be discussed below in relationship to points 2 and 3 above.

The dielectric effect, briefly mentioned by P–T, was originally calculated[29] by evaluating the stabilizing influence of a dielectric medium on the transition dipole. An alternative approach to this rather formal one is to consider the effect of a dielectric medium on the potential curves of the ground and excited states. This approach has the advantage that it displays the rather small over-all change which results from two large changes in the potential energy curve of the excited (CT) state. For weak EDA complexes where the CT interaction is small, the last term in eq 5 can be neglected and one can write

$$h\nu_{\mathrm{CT_{gas}}} - h\nu_{\mathrm{CT_{soln}}} = \left(I_{\mathrm{D}} - E_{\mathrm{A}} - \frac{e^2}{R}\right)_{\mathrm{gas}} - \left(I_{\mathrm{D}} - E_{\mathrm{A}} - \frac{e^2}{\xi R}\right)_{\mathrm{soln}} = -\left\{\frac{e^2}{R} - \frac{e^2}{\xi R}\right\} + \{(I_{\mathrm{D}} - E_{\mathrm{A}})_{\mathrm{gas}} - (I_{\mathrm{D}} - E_{\mathrm{A}})_{\mathrm{soln}}\} \quad (6)$$

Equation 6 is exact if the last term, $C_2/(I_{\mathrm{D}} - C_1)$, in eq 5 is the same, both in solution and in the gas phase.

The precise form of the correction (*i.e.*, the value of ξ) to the first term of eq 6, $-[(e^2/R)_{\mathrm{gas}} - (e^2/\xi R)_{\mathrm{soln}}]$, is not known. This is because the value of R in the equation is sufficiently small (3–5 Å) that the dielectric medium cannot be regarded as a homogeneous fluid. The macroscopically correct form of the correction is

$$-\left(\frac{e^2}{R} - \frac{e^2}{\xi R}\right) = -\frac{e^2}{R}\left(1 - \frac{1}{\xi}\right)$$

where ξ is the dielectric constant of the solvent. This equation will be used here to provide an approximate estimate of the energy involved. Substituting $R_{\mathrm{gas}} = R_{\mathrm{soln}} = 3.5$ Å and $\xi = 2$, one obtains

$$-\frac{e^2}{R}\left(1 - \frac{1}{\xi}\right) \cong -2.1 \text{ eV}$$

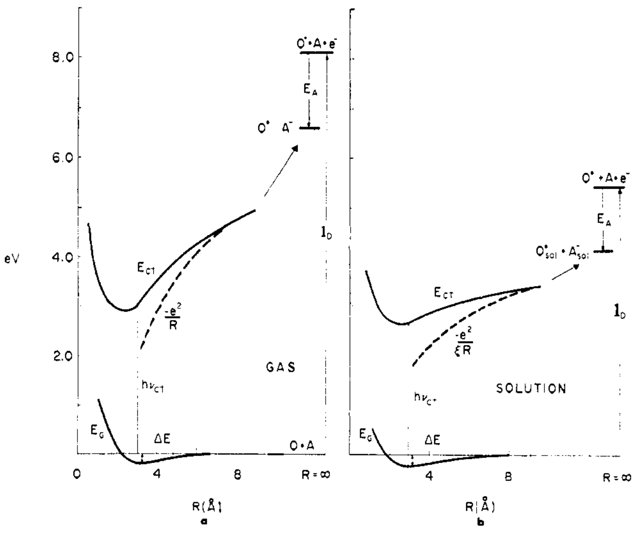

Figure 5. Energy level diagrams for gas-phase and solution EDA complexes. The vertical energy scale is rather arbitrary but more nearly approximates the case of the TCNE–EDA complexes than those of iodine.

The second term of eq 6, $[(I_{\mathrm{D}} - E_{\mathrm{A}})_{\mathrm{gas}} - (I_{\mathrm{D}} - E_{\mathrm{A}})_{\mathrm{soln}}]$, represents the difference in the separation of the potential levels of the infinitely separated molecules in solution and in the gas phase. Estimation of the magnitude of this term is facilitated by consideration of the thermodynamic cycles shown in Scheme I. In these

Scheme I

$$\begin{tikzcd}
\mathrm{D^S} \arrow[r, "I_{\mathrm{D}}^{\mathrm{S}}"] & \mathrm{D^{+S}} \arrow[d, "-\Delta H_{\mathrm{S}}(\mathrm{D^+})"] & + & \mathrm{e^{-S}} \arrow[d, "-\Delta H_{\mathrm{S}}(\mathrm{e^-})"] \\
\mathrm{D^G} \arrow[u, "\Delta H_{\mathrm{S}}(\mathrm{D})"] \arrow[r, "I_{\mathrm{D}}^{\mathrm{G}}"] & \mathrm{D^{+G}} & + & \mathrm{e^{-G}}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{e^{-S}} & + & \mathrm{A^S} \arrow[r, "-E_{\mathrm{A}}^{\mathrm{S}}"] & \mathrm{A^{-S}} \arrow[d, "-\Delta H_{\mathrm{S}}(\mathrm{A^-})"] \\
\mathrm{e^{-G}} \arrow[u, "\Delta H_{\mathrm{S}}(\mathrm{e^-})"] & + & \mathrm{A^G} \arrow[u, "\Delta H_{\mathrm{S}}(\mathrm{A})"] \arrow[r, "-E_{\mathrm{A}}^{\mathrm{G}}"] & \mathrm{A^{-G}}
\end{tikzcd}$$

cycles, S and G represent solution and gas phase, while $\Delta H_{\mathrm{S}}(\mathrm{X})$ indicates the heat of solution of species X. Appropriate combination of these cycles yields

$$\{I_{\mathrm{D}}^{\mathrm{G}} - E_{\mathrm{A}}^{\mathrm{G}}\} - \{I_{\mathrm{D}}^{\mathrm{S}} - E_{\mathrm{A}}^{\mathrm{S}}\} = \{(\Delta H_{\mathrm{S}}(\mathrm{D}) + \Delta H_{\mathrm{S}}(\mathrm{A})) - (\Delta H_{\mathrm{S}}(\mathrm{D^+}) + \Delta H_{\mathrm{S}}(\mathrm{A^-}))\} \quad (7)$$

The first term inside the braces is the sum of the heats of solution of the neutral molecules D and A. These heats will, in general, be small since they are the result of weak van der Waals forces. These include London dispersion forces in all cases, and in some cases they include dipole–dipole and dipole–polarization forces. If the solvent can serve as a donor, then solvent–acceptor EDA complexes must be included in this van der Waals energy. Tentatively, the sum of the heats of solution of the neutral molecules D and A can be estimated to be -0.1 to -0.2 eV.

The second term inside the braces can be estimated with the use of a formula originally derived by Born[30]

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(24) J. Ham, *J. Am. Chem. Soc.*, **76**, 3881 (1954).
(25) J. R. Gott and W. G. Maisch, *J. Chem. Phys.*, **39**, 2229 (1963).
(26) J. R. Stephens and H. G. Drickamer, *ibid.*, **30**, 1518 (1959).
(27) H. W. Offen, *ibid.*, **42**, 430 (1965).
(28) P. J. Trotter, *J. Am. Chem. Soc.*, **88**, 5721 (1966).
(29) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).
(30) M. Born, *Z. Physik*, **1**, 45 (1920).

$$\Delta G_S(x^{\pm}) = -\frac{e^2}{2R_x}\left(1 - \frac{1}{\xi}\right)$$

where R_x is the radius of a spherical cavity in a solvent having a dielectric constant ξ. Estimating a value of R_x is a rather arbitrary process;[31] however, setting $R_- = R_+ = 3$ Å with $\xi = 2$ as before, the value $\Delta G_{soln} \cong -2.4$ eV. Setting $\Delta G_{soln} \cong \Delta H_{soln}$ (a good approximation since the entropy change is expected to be small), the value of the quantity represented by eq 7 is +2.2 to +2.3 eV.

By this series of approximations, the value of $h\nu_{CT_{gas}} - h\nu_{CT_{soln}}$ is found to be 0.1 to 0.2 eV (800–1600 cm^{-1}). This is in reasonable agreement with the observed value of 1000–3000 cm^{-1}. It should, of course, be recognized that slight changes in the value of R_e'' as compared with R_+ and R_- could easily produce a shift opposite in direction to that observed, but, to the extent that the sum of the heats of solvation of the neutral molecules $\{\Delta H_S(D) - \Delta H_S(A)\}$ can be neglected, the solution red shift can be written

$$h\nu_{CT_{gas}} - h\nu_{CT_{soln}} = e^2\left(1 - \frac{1}{\xi}\right)\left(\frac{1}{R_x} - \frac{1}{R_e''}\right)$$

This predicts that as long as $R_x < R_e''$, *i.e.*, as long as the average ionic radius of the ions A$^-$ and D$^+$ is less than the equilibrium intermolecular separation in the ground-state R_e'', a red shift is expected on going to solution regardless of the magnitude of ξ. The above numerical estimates involve a number of approximations whose validity may be questioned; however, the basic point to be made here is that the relationship of the potential curves of the excited (CT) state of the complex is quite different in the two phases and that the two important electrostatic effects affecting the separation of the potential curves tend to cancel one another. These relationships are most readily visualized by comparing Figures 5a and b.

The consideration of the dielectric effect on the CT state leads to two further conclusions. First, the intermolecular equilibrium separation in the CT state will be different in the gas phase and in solution. By assuming that the potential curve of the CT state is the sum of a repulsive potential proportional to R^{-11} and an attractive coulombic potential proportional to $(\xi R)^{-1}$, one can estimate a value of $R_e'{}_{soln}/R_e'{}_{gas} \cong 1.07$ for $\xi = 2$ by evaluating R' when $(\partial V/\partial R) = 0$. Second, the CT absorption spectrum of the gas-phase complex should be broader than the solution spectrum because of the steeper slope of the CT potential curve in the gas phase. The magnitude of this broadening should depend on the difference between R_e'' and R_e' becoming greater as the difference increases. Examination of Tables I and II shows that the gas-phase spectra are broader, but only very slightly so, than the solution spectra.

The decrease in the red shift with increasing methylation of the donor molecule (see Table I) is explained by the bond compression model by saying that the stronger the complex (the strength of the complex as measured by $-\Delta H$ increases with methylation), the less compressible the bond is, and hence a smaller red shift is observed. The dielectric considerations suggest that, if for a series of complexes R_e'' is relatively constant, then the red shift ($h\nu_{CT_{gas}} - h\nu_{CT_{soln}}$) will decrease with increasing average ionic radius R_x. Therefore, one expects a decrease in the red shift with increasing methylation.

It was estimated that the first term inside the braces of eq 7 was -0.1 to -0.2 eV; *i.e.*, the neutral molecules D and A are stabilized on going to solution. It is interesting to consider what effect these solvation energies should have on the ΔE of complex formation. At infinite separation, the ground-state molecules D and A are each surrounded by a cluster, or shell, of solvent molecules S. To allow the closest approach of the D and A molecules on complex formation, one or more molecules must be removed (excluded). To remove these molecules, energy must be supplied, but, when the solvent molecules excluded enter the main body of the solvent, an equal number of solvent bonds (S–S bonds) are formed. Since all these bonds are van der Waals bonds between molecules of comparable dimensions, one expects the bond energies to be quite similar, and it is therefore reasonable to expect that they approximately cancel one another in solution. In the vapor, however, the van der Waals bond energy between the D and A molecules must simply add to the CT stabilization energy of the ground state. This should result in a larger value of $|\Delta E|$ for the complex in the gas phase than in solution.

The preceding discussion has tacitly assumed that the complex has the same configuration in the gas phase as in solution. This may not be a valid assumption as was pointed out in the discussion of the spectral shift, where a decrease in the intermolecular separation was expected (according to P–T) on going to solution. However, if the van der Waals energies are added to the CT stabilization energy in the gas phase, one expects a decrease in the intermolecular separation on going to the gas phase. Furthermore, the increased importance of the van der Waals energies in the gas phase might cause the most stable conformation of the ground state to differ between the two phases. This should not be so important in the case of π–π complexes (such as the TCNE complexes with aromatic hydrocarbons) since a sandwich-type structure should favor both the van der Waals and CT energies, but in the case of n–σ complexes (such as the organic sulfide complexes with iodine) van der Waals energies may be favored by structures which are not the most favorable structures for CT interaction. More specifically, one might guess that CT interaction would be favored by a structure for the sulfide–iodine complex in which the internuclear axis of the I_2 molecule is perpendicular, or nearly so, to the plane containing the C–S–C atoms at the sulfur atom, whereas van der Waals energies may be most favored by having these two axes perpendicular to each other in such a way that both iodine atoms are in close contact with the sulfur atom instead of the observed arrangement in crystals in which only one iodine atom is in close contact with the sulfur atom. It has also been suggested by Rice[32] that free rotation of the molecules in the gas phase should decrease the average CT interaction energy for a pair of molecules because rotation should prevent the most favorable orientation of the partners. It is widely assumed that free rotation in the gas phase is reduced to libration on going to solution. Finally, the bond compression model of P–T predicts that the

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(31) E. J. W. Verwey, *Rec. Trav. Chim.*, 61, 127 (1942).

(32) Private communication from O. K. Rice to R. S. Mulliken.

$|\Delta E|$ value in solution should be greater than the gas-phase value because the increased overlap should cause greater CT stabilization of the ground state. The above discussion shows how difficult it is to arrive at a reliable explanation or prediction of differences between ΔE values in the gas phase and in solution.

However, in the case when the structures are the same in both phases, one expects an increase in the value of $|\Delta E|$ in the gas phase as compared with the solution value. This is precisely what is observed for the TCNE complexes, which are not expected to change conformation between the two phases. The same result is obtained[33] in studies of gas-phase hydrogen-bonded dimers of carboxylic acids. It is generally accepted that carboxylic acid dimers have very similar structures in the gas phase and in solution. The EDA complexes of organic sulfides with iodine, in contrast to the two above examples, show little change in the value of ΔE between the two phases.

The relationship between gas-phase and solution absorption intensities is at present not well understood. A simple formulation[34] predicts a moderate increase in intensity on going to solution, but experiments[35,36] have not always borne this out. It has been stated[6,28] that the cage effect of solvents should increase the CT absorption intensity because of the increase in overlap integrals of donor and acceptor orbitals when the intermolecular separation decreases. The possibility of free rotation of one partner (*e.g.*, I_2) if it occurs in the gas phase, by preventing favorable orientation for CT interaction, should also decrease the CT absorption intensity of EDA complexes.[32] One discussion[37] of solvent competition with donor for acceptor molecules has suggested that in solution the extinction coefficient is overestimated and the equilibrium constant is underestimated by factors of 10 to 20; however, this discussion seems to assume considerable donor strength for the solvent molecules which is not the case for inert solvents like heptane. Furthermore, eq 1 and 2 assume unit activity coefficients for all species D, A, and D–A. It has been shown[38] that, for the case of the benzene–I_2 complex (using the data of ref 10), the values of $\epsilon_{\max}$ for the CT band vary from 9800, if the concentrations in eq 1 are expressed in molal units, to 18,000, if the concentrations are expressed in mole fraction units. Thus the large differences between gas-phase extinction coefficients and those evaluated in solution may at least in part be due to inadequacies in the interpretation of the solution data for EDA complexes. This point requires further clarification.

Next, the greatly reduced intensity in, or possible lack of, the blue-shifted visible iodine absorption band requires attention. It should be pointed out that the discussion of the preceding paragraph concerning the approximation of unit activity coefficients for all species D, A, and D–A applies equally as well to the evaluation of the extinction coefficient of the blue-shifted iodine band. The decrease in the absorption intensity of the blue-shifted band by a factor of ~10, as measured by the ratio ϵ(unshifted)/ϵ(blue-shifted) in the two phases, is of the same order of magnitude as the decrease in the intensity of CT absorption. Therefore, part of the decrease in intensity of the blue-shifted iodine band may be due to the activity coefficient approximation; however, there may be structural differences between EDA complexes in the two phases, as discussed above, which can further contribute to the observed intensity decrease.

The visible absorption system of iodine is caused by absorption of light which promotes an electron from a bonding σ_g MO in the ground state of iodine to an antibonding σ_u MO in an excited state of iodine. Mulliken[39] has explained the blue shift observed in solution spectra of EDA complexes as being due mainly to exchange repulsion between the iodine molecule in the excited state and the nearby donor molecule. This is expected because the antibonding orbital of the excited state has a larger effective size than the outermost filled ground-state orbitals. Since the increase in the effective size of the outer MO on excitation is not spherically symmetrical, the relative orientation of the donor and the iodine molecule in the ground state of the complex is important in determining the magnitude of this effect. A donor molecule (*e.g.*, R–S–R) located along the internuclear axis of I_2 should cause more exchange repulsion than a donor molecule in a plane perpendicular to and bisecting this axis. Also, the exchange repulsion should increase the closer the contact of the donor and iodine molecules. Thus, a change in the ground state of the complex should lead to a decrease in the magnitude of the blue shift. If the change in the ground-state conformation in the gas phase as compared with the ground-state conformation in solution is pronounced, the blue shift might even become unobservable. Also, the free rotation of the I_2 in the complex may decrease the exchange repulsion and thereby decrease the intensity of the blue-shifted band. The above discussions are advanced as possible explanations of the observations of this work, although other types of iodine complexes will have to be studied in the gas phase to provide a definite answer to this question.

Finally, the appearance of two maxima in the absorption spectra of *p*-xylene with TCNE and of durene with TCNE warrants some discussion. The appearance of two maxima in the CT absorption spectra is characteristic of these two complexes in both solution and the gas phase. This has been interpreted by Orgel[40] as being caused by the splitting in *p*-xylene and durene of the ionization energies of the π orbitals which in benzene are degenerate. The observation that the separation of the two peaks is nearly the same in both the gas phase and in solution[3b] supports this idea.

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(33) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(34) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

(35) L. W. Pickett, E. Paddock, and E. Sackter, *J. Am. Chem. Soc.*, **63**, 1073 (1941).

(36) L. E. Jacobs and J. R. Platt, *J. Chem. Phys.*, **16**, 1137 (1948).

(37) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).

(38) P. J. Trotter, and M. W. Hanna, *J. Am. Chem. Soc.*, **88**, 3724 (1966).

(39) R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).

(40) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).