

were measured on the same sensitivity scale of the electrometer and the precision of individual peak-intensity measurements was 0.2% or better. This accuracy was not possible with the conventional strip-chart recorder which gave errors of up to 1% for the most favorable peak-height ratios. Effects of fluctuations in beam intensity during a sweep were overcome by averaging the results of 10 or more successive sweeps taken over a period of 15 or more minutes.

The results obtained from approximately 2500 determinations of isotopic ratios taken with three different sample systems and several samples having compositions covering the range from about 25 to 75 at. % D gave values of 3.74 ± 0.02 at 0° and 3.76 ± 0.02 at 25° . Equilibria at elevated temperatures were measured using a heated sample and inlet system; at 75° , values of 3.80 ± 0.04 were obtained. Values at much higher temperatures were not successfully determined because of the difficulty of establishing and maintaining equilibrium at these temperatures. The temperature coefficient is real even though the absolute errors quoted overlap the range of temperature variation observed.

These results are to be compared with values of K_1 of 3.83 (0°), 3.85 (25°), and 3.89 (75°) calculated in the harmonic approximation using the computer program of Wolfsberg and Stern⁸ and the complete harmonic force field of Papoušek and Plíva.³ The values of 3.4–3.5 obtained from calculations that have included corrections for anharmonicity based on recent spectroscopic results² are clearly not in agreement with our experimental data. Theoretical aspects of this problem will be discussed in a separate publication by Wolfsberg.

We are indebted to Dr. Wolfsberg for making the computer program available to us and to him and Dr. Bigeleisen and Dr. Weston for many stimulating discussions. We also wish to express our appreciation to Professor F. A. Long for valuable comments in review of this letter. One of us (V.J.S.) wishes to express his gratitude to the Brookhaven National Laboratory and its Chemistry Department for their hospitality during the tenure of his sabbatical leave there.

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Notes

Partial Ionization Cross Sections of He, Ne, H₂, and CH₄ for Electrons from 20 to 500 eV

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RECENTLY Schram *et al.*¹ reported measurements on the partial ionization cross sections of He and Ne, performed on a mass spectrometer. A serious drawback of this instrument is the very bad ion transmission from the source to the collector, giving rise to unpredictable discriminations in collection efficiency for the different ions.

For singly and multiply charged ions of noble gases the initial kinetic energy is negligible. Therefore, Schram *et al.* were able to ascertain, by special precautions, a constant transmission for the ions under consideration. For fragment ions of molecular gases, however, the usual mass spectrometer is unable to give reliable results.

With our newly designed cycloidal mass spectrometer,² it is possible to attain a complete collection of all ions produced in the source, and absolute measurements of the ionization cross sections should be possible.

This mass spectrometer did not have slits in the source; the electron beam moved freely in space. The collector slit was 2 mm wide, the distance from the source to the collector was 126 mm. The resolving power was 40 (theoretical value 50).

We measured the ionization cross section for electrons from 20 to 2000 eV of He, Ne, H₂, and CH₄. Parent and fragment ions were measured, as well as multiply charged ions. As a real ionization chamber does not exist, the pressure in the ionization region is essentially the

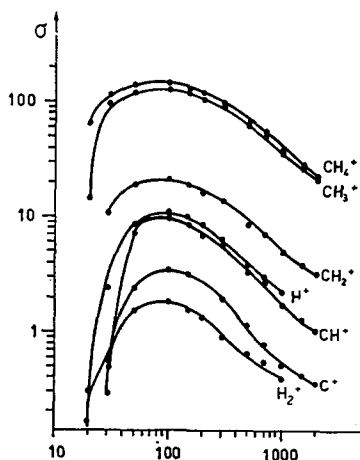


FIG. 1. The partial ionization cross section of methane ($\times 10^{-18}$ cm²/molecule).

TABLE I. Partial ionization cross sections of He, Ne, and H₂ in 10⁻¹⁸ cm²/atom.

E_{el} in eV	He ⁺	He ²⁺	Ne ⁺	Ne ²⁺	Ne ³⁺	H ⁺	H ₂ ⁺
20	0.118	24
30	4.9	...	7.6	0.71	58
50	17.5	...	25	1.68	81
70	25	2.1	86
100	29	0.0109	52	0.52	...	2.0	80
150	29	0.059	57	1.92	...	1.76	71
200	27	0.091	57	3.1	...	1.56	62
300	23	0.106	0.110	1.08	48
400	18.8	0.096	0.91	41
500	16.4	0.088	41	2.1	0.115	0.75	33
600	15.0	0.076	0.67	29
700	13.2	0.068	33	...	0.090	0.62	26
800	12.4	0.060	0.55	24
900	11.4	0.052	0.52	23
1000	11.0	0.048	27	1.31	0.068	0.49	21
1500	21	0.89	0.046
2000	16.9	0.70	0.036

same as in the whole separation box. Now for sufficient ion intensity a high pressure is wanted in the ionization region, whereas a low pressure is necessary along the ion paths, to avoid loss of ions by charge exchange or scattering processes. As the peak height, as a function of the pressure, shows a linear behavior up to 10⁻⁴ torr for most ions, all measurements were performed at 2×10⁻⁵ torr. Also a proportionality of the peak height with the ionizing electron current was observed.

The results of the partial ionization cross sections for electrons on He, Ne, H₂, and CH₄ are given in Tables I and II. Moreover the results on CH₄ have been plotted in Fig. 1. In order to avoid a precise pressure measurement, we normalized the sum of our ion intensities at 200-eV electron energy (for CH₄ at 600 eV) on the value of the gross ionization cross sections reported by Schram *et al.*^{3,4} Below 500-eV impact energy, this normalization factor was apparently constant, consequently we assume our partial ionization cross sections to be substantially correct below this electron energy. Above 500 eV we found that the normalization factor decreased to about 20% low at 2000 eV. This difference is probably caused by secondary electrons in the source of the mass spectrometer,

as not sufficient precautions were taken to suppress them in the preliminary setup.

Our values of the relative abundance of He²⁺ with respect to He⁺, and the relative abundance of Ne²⁺ and Ne³⁺ with respect to Ne⁺, were within about 20% from the values obtained by Schram *et al.*,¹ which seems reasonable, when we consider the different instruments and measuring techniques.

The results on CH₄ at 50 and 70-eV electron impact energy agree very well with the data on the A.P.I. tables,⁵ except for H⁺ and H₂⁺, where our values are substantially higher.

Recent literature values for H⁺/H₂⁺ range between 1.2%⁶ and 6.3%⁷ at 100-eV electron energy. The A.P.I. tables give 2.1%.⁸ We assume these large differences are caused mainly by energy discrimination.

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This work is part of the research program of the

TABLE II. Partial ionization cross sections of methane in 10⁻¹⁸ cm²/molecule.

E_{el} in eV	H ⁺ m=1	H ₂ ⁺ 2	C ⁺ 12	CH ⁺ 13	CH ₂ ⁺ 14	CH ₃ ⁺ 15	CH ₄ ⁺ 16
20	0.165	0.31	14.6	64
30	2.48	0.57	0.29	0.49	10.6	96	114
50	8.5	1.55	2.5	9.0	19.9	121	141
100	11.3	1.89	3.5	9.7	21	126	145
150	9.9	1.57	3.3	8.5	19.2	116	129
200	8.6	1.34	...	6.9	16.1	104	118
300	6.4	0.92	1.97	5.7	13.9	88	98
500	3.9	0.67	1.16	3.3	8.6	62	77
700	3.1	0.57	0.81	2.7	7.2	49	57
1000	2.3	0.41	0.52	1.74	5.0	36	38
1500	0.42	1.31	3.9	26	28
2000	0.36	1.04	3.2	21	23

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Spectral Shifts in the Absorption Spectra of EDA Complexes in Solution

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THE general concepts of solvent shifts¹⁻⁹ have been profitably applied to predicting the direction of shift in solvents of different polarities and to estimating excited-state dipole moments μ_e , when this quantity represents a large change from its value in the initial state (μ_0). The purpose of this report is to test the applicability of current theories of solvation to electron-donor-acceptor (EDA) complexes in solution. From spectral shifts in the absorption and emission, the excited-state dipole moment has been determined for dyes by Lippert⁴ and for the hexamethylbenzene-tetrachlorophthalic anhydride (HMB-TCPA) complex by Czekalla and Meyer.¹⁰ Since none of the other EDA complexes investigated here displayed measurable charge-transfer (CT) fluorescence in liquid solutions, their method could not be further tested. However, Basu^{7,8} developed a theory, based on the Onsager continuum model, which permits the estimation of μ_e of solutes in nonpolar solvents only from spectral shifts in the absorption spectra. Basu and Chakrabarti¹¹ applied their formula to aromatic-hydrocarbon-tetrahalogenated benzoquinone complexes and calculated μ_0 , μ_e , and vapor-phase CT transition energies.

The present work reports spectral shifts in the absorption spectra of TCNE (tetracyanoethylene) and TCPA complexes with representative aromatic hydrocarbons (ArH) in several solvents at room temperature.

The CT absorption-band maxima are collected in Table I. Where comparison with other measurements¹²⁻¹⁵ is possible, agreement within ± 0.2 kK is obtained. Broad bands which could not be assigned within this accuracy are so indicated in the table. TCNE complexes with naphthalene, pyrene, and fluorene show two broad maxima which result from complex formation. The absorption spectra were measured at least twice with the Cary Model 14 spectrophotometer.

There is no correlation between the magnitude of the shift and the refractive index n or dielectric constant ϵ of the solvent, but the CT-band maxima in polar ethyl acetate, cyclohexanone, and acetone lie considerably higher than in the other solvents. Assuming that the band origin behaves similarly, the direction of shift for both these weak and strong complexes is opposite to that generally observed in polar media for one-component solutes in which the dipole moment increases upon excitation.^{1-9,16,17} The observed red shift for the latter systems ($\mu_e \gg \mu_0$) is predicted by previously advanced solvent-shift theories which propose that the solvation free energy of the highly polar state is much larger in polar media (dipolar and dispersive interactions) and therefore the transitions show a net displacement to lower energies. For the complexes discussed here it is accepted^{18,19} that the ground state of the complex is weakly polar ($\mu_0 \sim 1$ D for nonpolar ArH-nonpolar TCNE complexes²⁰), while the excited state is largely an ion pair due to the intermolecular charge transfer in the CT transition ($\mu_e \sim 12$ D).¹⁰ Hence a red shift might have been expected.

The experimental fact that increasing the polarity of the solvent results in larger separations of the CT states in these systems is clearly not in accord with general solvent-shift theories ($\mu_e \gg \mu_0$). From recent vapor-phase measurements^{21a,b} it is clear that an initial red shift occurs in nonpolar solvents. For the HMB-TCNE complex, $h\nu_{CT}$ are comparable in acetone and the vapor phase.^{21b} Yet Basu applied his theory of dipolar interaction^{7,8} to ArH-tetrahalogenated benzoquinone complexes¹¹ and obtained reasonable μ_e values by reversing the direction of shift in nearly nonpolar solvents. By employing the same artifice of sign reversal, Basu's equation applied to the present systems gives reasonable values for μ_e (12–15 D), evaluated from simultaneous equations representing CT energies in the solvents carbon tetrachloride, chloroform, and ethyl acetate. For example, $h\nu_{CT}$ (vapor) = 31 kK and $\mu_e = 12$ D (the value obtained for HMB-TCPA¹⁰ from Lippert's theory⁴ is $\mu_e = 14 \pm 3$ D) is calculated when 4.5 Å is chosen as the cavity radius. Of course, such approach has no merit from a theoretical standpoint.

Several explanations can be advanced to account for the vapor-nonpolar-solution red shift and the nonpolar-polar-solution blue shift. Specific interactions between the complex and the surrounding environment opposing the general red shift⁶ are evidently most significant in these systems. Czekalla and Meyer¹⁰ men-