

TABLE I. Angular dissymmetry of a van der Waals gas (with $K^2=5\times 10^{-6}\text{ \AA}^{-2}$, $l^2=30\text{ \AA}^2$, and $T_c=304.19^\circ\text{K}$).

ϕ ($=V/V_c=\rho_c/\rho$)	x		
	$\Delta T=0.005^\circ$	$\Delta T=0.01^\circ$	$\Delta T=0.05^\circ$
0.96	1.02	1.02	1.02
0.93	1.08	1.07	1.05
0.99	1.27	1.23	1.10
1.00	2.52	1.76	1.15
1.02	1.08	1.08	1.05

to approach the critical point because the pressure must be measured with high accuracy in order to specify the density even moderately well near the critical point. If the pressure and temperature are used to specify the system, it will appear to be near the critical point, when in fact, it is not.¹⁰ For example, in the case of argon,³ at $P/P_c=0.999$, and $T-T_c=0.05^\circ$, we find that $\rho/\rho_c=0.915$. Thus, it is more appropriate to use density as one of the two thermodynamic variables for specification of the system.

In principle, we may approach the critical point by performing our experiments at the critical pressure and at decreasing temperature distances from the critical temperature. In practice, such an approach is not only difficult but unrealistic. We illustrate our point by examining the isotherms of carbon dioxide, measured by Michels and his co-workers,¹¹ as shown in Fig. 1. At or near the critical density, a small fluctuation in pressure, say ± 0.25 psi, or $\pm 0.023\%$, produces a large change of the density which amounts to 33 amagat, or 14%, when $T-T_c=0.15^\circ$. Hence, it is not appropriate to use an apparatus in which only a small portion of the total sample is maintained in the critical region.

As the critical point is approached even more closely, the effects of the isothermal compressibility become increasingly insidious. There, gravity causes an appreciable density gradient to develop along the height of the cell and scattering measurements get smeared whenever beam heights are appreciable. In addition, the density of the sample at any given height will change as the critical temperature is approached.

We shall estimate the effect of the density on the scattering behavior of a van der Waals gas using a modified Debye theory¹²:

$$I^{-1} \propto 1 + \frac{K^2 l^2}{6\{[4\phi^3\tau/(3\phi-1)^2]-1\}} = x,$$

where I is the scattered intensity, $K=(4\pi/\lambda)\sin\frac{1}{2}\theta$, l is the Debye interaction parameter, $\phi=V/V_c=\rho_c/\rho$, and $\tau=T/T_c$. If we take $K^2=5\times 10^{-6}\text{ \AA}^{-2}$, $l^2=20\text{ \AA}^2$, and $T_c=304.19^\circ\text{K}$, we see that the angular dependence of scattered light falls off sharply when the system moves away from the critical density, as shown in Table I. Thus it is difficult to determine the angular dissymmetry of scattering by means of visible light

whenever ρ is away from ρ_c because of the shorter range of K in the visible-light scattering range when compared with small angle scattering of x rays. Nevertheless, light-scattering measurements should remain one of the best means to obtain relative isothermal compressibilities from extrapolated zero-angle scattered intensities.

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⁹ Research in progress; initial results to be published in the near future.

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Polarized Triplet-Triplet Absorption in Charge-Transfer Complexes

KENNETH B. EISENTHAL

IBM San Jose Research Laboratory, San Jose, California

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THE determination of the polarized triplet-triplet absorption is used in this work as a new approach to probe the effects of complexing on the triplet states of donor molecules. This method permits an examination of the changes due to complexing within the triplet manifold itself. The donor's phosphorescence, on the other hand, involves only the lowest triplet-state emission and is thus more importantly dependent on the singlet-triplet vs the triplet-triplet interactions in the complex. The perturbations on the lowest triplet state of the donor as a result of complexing have received considerable attention.¹⁻⁵ A marked increase in the donor triplet to ground radiative transition⁴ and, for some molecules, significant changes in the vibrational character of the phosphorescence⁵ have been observed.

The systems studied were the complexes of naph-

thalene- d_8 and phenanthrene- d_{10} with TCPA (tetrachlorophthalic anhydride) in the EPA glass at 77°K. These complexes were selected for several reasons. First, their triplet emissions have been carefully studied¹⁻³; second, the triplet-triplet absorption spectra of the uncomplexed donors are known.^{6,7} The naphthalene-TCPA complex is particularly interesting on two points: (1) the variation in the polarization of the vibronic bands in the $T \rightarrow S_0$ transition in the complex (a variation which is absent in the uncomplexed-donor phosphorescence) suggests the possible mixing of triplet states in the complex³; and (2) the assignment of the higher excited triplet as the ${}^3B_{3g}$ in the free molecule was limited by the fact that absorption into the lowest singlet states is primarily along the short axis due to 1L_a and 1L_b mixing.⁸ In the charge-transfer complex it is possible to excite in a different direction, i.e., perpendicular to the naphthalene plane, by absorption into the lowest singlet charge-transfer band. Thus, the assignment of the higher triplet as the ${}^3B_{3g}$ can be checked.

Excitation into the charge-transfer band at 3660 Å was effected with a 500-W Hg lamp. The triplet-triplet absorption was obtained with a tungsten source, detected with a 6256S EMI photomultiplier, and recorded using a $\frac{3}{4}$ -m Czerny-Turner spectrometer. The tungsten source and spectrometer were on line, and the Hg source was at right angles with respect to this direction. A Glan-Thomson polarizer and a polaroid-sheet analyzer were used in the polarization experiments. The precision of the measured degree of polarization is ± 0.01 . The energy separation of the first two bands in each of the complexes was the same as the separation in the free molecules (~ 1500 cm⁻¹). The polarization and energies in the complex are shown in Table I.

The relatively low polarization values are due to depolarization effects in the apparatus and the wavelength of excitation. (See Ref. 3 concerning this latter point.)

Because of the proximity of the exciting wavelength to the naphthalene 3710-Å band, the polarization of this band was not determined.

Phenanthrene: The polarization of the T-T band in the free molecule has been shown to be in the direction of the long axis of phenanthrene.⁸ Assuming that the lowest triplet of phenanthrene is weakly perturbed by complexing (as assertion supported by the phosphorescence data), then the polarization of the triplet-triplet absorption should be negative with respect to excitation into the singlet charge-transfer band since the latter absorption is polarized perpendicularly to the phenanthrene plane. This is found to be the case, and this result is, therefore, consistent with the long-axis assignment.

Naphthalene: Although the direct mixing of excited states which have different polarizations with respect to transitions to the ground state is possible because

TABLE I. Degree of polarization of triplet-triplet absorption on excitation into the charge-transfer band.^a

Naphthalene- d_8		Phenanthrene- d_{10}		
4848 Å	3905 Å	4920 Å	4580 Å	4310 Å
-0.076	-0.13	-0.11	-0.12	-0.12

^a Degree of polarization = $(\epsilon_{||} - \epsilon_{\perp}) / (\epsilon_{||} + \epsilon_{\perp})$, where ϵ is the molar extinction coefficient.

of the reduced symmetry of the complex, phosphorescence data indicates that for the complexes of the polyacenes with TCPA this mixing is not significant. With this assumption, the excitation into the new band produced by the formation of the charge-transfer complex must yield a negative triplet-triplet polarization in order to agree with the T-T long-axis absorption postulated for the free molecule.⁸ This, indeed, is found to be the case. Thus, the excited triplet in free naphthalene is ${}^3B_{3g}$. This method of excitation into the charge-transfer band should prove of some aid in the assignment of excited triplet states.

The polarization of the 0-0 triplet-triplet absorption band at 4148 Å is found to be significantly different from that of the band at 3905 Å (Table I). If there were direct electronic mixing without vibronic interactions between the donor triplet states and the charge-transfer or acceptor states (made possible because of the low symmetry of the complex) one would expect this to be equally reflected in both vibronic bands. Since there is a marked difference in the polarization of the two bands, the latter possibility can be rejected as a plausible explanation for this disparity. The observed variation in the polarization of these bands is more likely due to vibronic mixing with some triplet state or states having different symmetries and, therefore, leading to different T-T polarizations. This difference in the polarizations is consistent with the variations found in the polarization the phosphorescence bands³ and, thus, supports the possibility of the vibronic mixing between the triplet states of the complex.

A possible reason for the similar polarizations found for the phenanthrene bands versus the different polarizations found for the naphthalene bands may be the stronger T-T absorption in phenanthrene.^{6,7} Thus, the vibronic mixing, if it occurs in phenanthrene, would have a less pronounced effect on the polarizations of the T-T bands.

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