

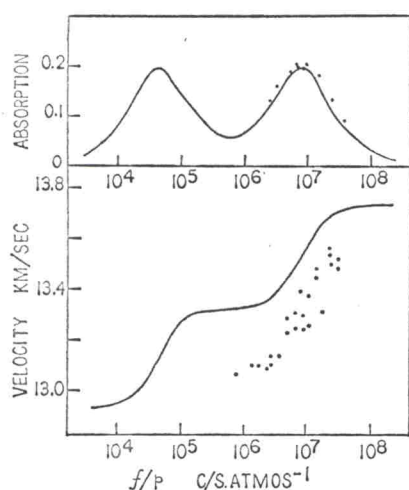


FIG. 1. Calculated ultrasonic absorption (Nepers/wavelength) and velocity for CH_2Br_2 . Experimental points from reference 1.

dispersion region involving the specific heat contributions of all modes except the lowest. In particular, since modes 2 and 3 differ in frequency by only 61 cm^{-1} , it is very unlikely that they should be associated with different relaxation times (contrast Meyer's assignment).

A calculation of the predicted relaxation behavior for this molecule has been carried out by the method described by Tanczos,² extended in an obvious way to take account of transitions involving up to four vibrational quanta. Lennard-Jones intermolecular force parameters for CH_2Br_2 were not available, and estimated values of $\epsilon/k=450^\circ\text{K}$, $r_0=5.06 \text{ \AA}$ were used; these are consistent with the viscosity coefficient used by Meyer. The shape of the dispersion curve was found to be relatively insensitive to the actual values of ϵ and r_0 chosen. The sound velocity a and the amplitude absorption coefficient α were calculated through the expressions

$$(a/a_0)^2 = 1 + \sum_i \frac{D_i(\omega\tau_i)^2}{1 + (\omega\tau_i)^2}$$

$$(\alpha/\omega)(a/a_0)^2 = 2a^{-1} \sum_i \frac{D_i\omega\tau_i}{1 + (\omega\tau_i)^2}$$

where ω is the angular frequency, and τ_i and D_i are the effective relaxation times and associated constants as defined by Tanczos.² Values of these were found to be $\tau_1=3.5 \times 10^{-6} \text{ sec}$, $D_1=0.0632$ (corresponding to specific heat $C_1=1.630R$); $\tau_2=1.9 \times 10^{-8} \text{ sec}$, $D_2=0.0662$ ($C_2=0.942R$). The remaining relaxation times were associated with negligible D 's.

The plot of calculated absorption (Fig. 1) agrees well with the experimental points of reference 1. The dispersion curve differs from the experimental points in two main respects: (i) there is no dispersion predicted at $f/p > 50 \text{ Mc/atm}$; (ii) the shorter relaxation

time is associated with the specific heat of mode 1 alone, the contributions of other modes having dropped out at lower frequencies. There is thus a fundamental disagreement between theory and experiment for this molecule, which further experimental work covering wider frequency range might resolve.

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Effect of Pressure on the Electronic Absorption Spectra of Ferrocene and Ferricinium Ion*

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THE effect of pressure has been measured on the electronic absorption peak near 24000 cm^{-1} of ferrocene $[(\text{C}_5\text{H}_5)_2\text{Fe}]$, and of two derivatives of ferrocene $[(\text{C}_5\text{H}_4\text{CH}_3)_2\text{Fe}]$ and $[(\text{C}_5\text{H}_4\text{SO}_3\text{Na})_2\text{Fe}]$. The peak of the ferricinium ion in ferricinium fluosilicate near 16000 cm^{-1} has also been studied. The samples were studied as crystallites distributed in NaCl. The high-pressure optical techniques have been described previously.^{1,2}

Figure 1 shows the shift of the peak maximum for ferrocene and its derivatives. There is a blue shift of the peak which is quite independent of the compound involved. According to Yamazaki³ the most probable assignment for this transition is $A_1' \rightarrow A_2''$ for D_{5h} symmetry (or $A_{1g} \rightarrow A_{2u}$ for D_{5d} symmetry). The shift would then be from a $3d$ level (or $3d-4s$ hybrid) to the $4p_z$

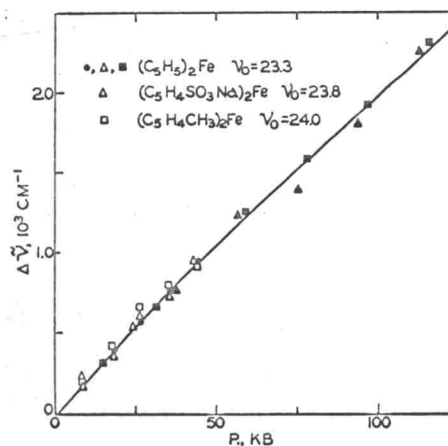


FIG. 1. Shift of peaks vs pressure, ferrocene and derivatives.

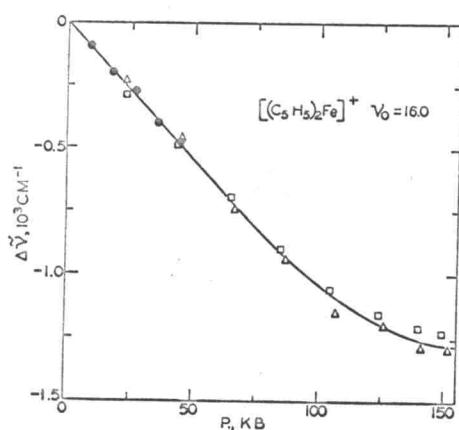


FIG. 2. Shift of peak vs pressure, ferricinium fluosilicate.

state. This assignment is not inconsistent with the discussions of ferrocene energy levels by Moffitt,⁴ Dunitz and Orgel,⁵ or Liehr and Ballhausen.⁶

It would also seem reasonable that the energy of the p_z state would be increased with increasing compression due to repulsion interaction with the cyclopentadiene electrons.

Figure 2 shows the shift of the 16 000-cm⁻¹ peak in ferricinium ion. The peak shifts to the red (to lower energies) with increasing pressure, with a distinct degree of leveling of the shift at high pressure.

As yet, there have been, to our knowledge, no quantitative treatments of the energy levels of the ferricinium ion. Dunitz and Orgel⁴ point out that the metallic levels must be somewhat stabilized vis-a-vis the cyclopentadiene levels. Second, they point out that the positive charge is probably distributed over the cyclopentadiene rings. In this case the excited state could then still be a metallic $4p_z$ level. At least at low pressures the energy of this level would be lowered by compression because of increasing interaction with the positively charged rings. The leveling could be due to ultimate overlap with the ring electrons. The situation would, in a qualitative way, be analogous to the situation in solid nickel dimethylglyoxime and related chelates, where a red shift followed by a leveling (and ultimate reversal) has been assigned to a $3d \rightarrow 4p_z$ transition.⁷

In the absence of a quantitative treatment these assignments must be regarded as tentative, but not unreasonable. In particular, the possibility of charge transfer, in the case of ferricinium ion, has not been eliminated.

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Depolarization of Scattered Light by n -Paraffin Vapors and the Additivity of Bond Polarizability Tensors*

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THE principle of additivity of bond polarizability tensors is controversial.¹⁻⁶ The difference between values of the C—C bond anisotropy obtained from vapor-phase and crystal measurements and on comparing birefringence values of polyethylene and polypropylene films have been ascribed to deviations from additivity resulting from internal field effects.⁴ In order to evaluate these effects more critically, a careful measurement of the depolarization of the scattering of a series of n -paraffins up to heptane was undertaken.⁶

Measurements were conducted⁶ by enclosing the vapors in a Teflon-lined brass Rayleigh cross of about 3-in. diam cross section provided with optical thermal glass windows and surrounded with an oil jacket for thermostating. Parallel incident light (0.35° divergence) originating from an Osram HB0109 100-w dc mercury arc was used. Parallel scattered light was po-

TABLE I. Depolarizations and anisotropies.

Substance	ρ (meas) $\times 10^3$	ρ (lit) $\times 10^3$	γ (A) ³	C (theory)	$\Gamma_{CC}(\text{exptl})$ (A) ³
CO ₂	8.47 ± 0.03	9.8 ^a 7.24–9.72 ^b	...	...	...
Ar	0.17 ± 0.02	0.42–0.56 ^b 0.5 ^a	...	...	...
N ₂	2.48 ± 0.06	3.6 ^a	...	...	...
ethane	0.77 ± 0.02	0.5 ^b 1.6 ^a	1.09	1.00	1.09
n -propane	0.94 ± 0.02	0.7 ^b 1.6 ^a	1.73	1.15	1.50
n -butane	1.02 ± 0.02	0.9 ^b 1.7 ^a	2.28	1.63	1.42
n -pentane	1.23 ± 0.02	1.3 ^a 1.2 ^c	3.17	1.93	1.64
n -hexane	1.64 ± 0.01	1.5 ^a 1.56 ^c	4.28	2.33	1.84
n -heptane	2.00 ± 0.06	1.6 ^a 1.4 ^c	5.24	2.59	2.09

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^c H. A. Stuart, *Die Physik der Hochpolymeren* (Springer-Verlag, Berlin, 1952), Chap. 6, Vol. I.