

Diffuse Spots of Pyrene at Higher Temperatures

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first substituent is *ortho-para* directing then a red shift is produced by the *para* substituted fluorine.

Bands in the weak portion of the spectrum have been associated with upper state frequencies of 147, 361, 499, 616, 794, and 1177 cm^{-1} . Also bands representing ground state frequencies of 178, 537, 644, 838, 1023, and 1242 cm^{-1} have been measured. Only broad diffuse bands are found in the strong absorption around 2200 Å. This transition is interpreted as an A_1-A_1 transition with the 0,0 band at 44 080 cm^{-1} . Further study of the spectrum is in progress at the present time.

¹ J. R. Platt, *J. Chem. Phys.* **19**, 263 (1951).

² *Catalog of Ultraviolet Spectrograms*, American Petroleum Institute Research Project 44, National Bureau of Standards (1945-1950), Serial No. 26 contributed by the Union Oil Company Serial No. 40 contributed by the Shell Development Company.

³ R. C. Hirt and J. P. Howe, *J. Chem. Phys.* **16**, 480 (1948).

⁴ W. T. Cave and H. W. Thompson, *Disc. Faraday Soc.* **9**, 35 (1950).

⁵ H. Sponer, *Phys. Rev.* **87**, 213 (1952).

Nuclear Quadrupole Resonance in Some Metal Chlorides and Oxchlorides

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(Received December 8, 1952)

ABSORPTION lines due to nuclear quadrupole resonance¹ of the chlorine isotopes Cl^{35} and Cl^{37} have been detected in the compounds given below. As the chlorine atoms occupy different sites in the crystal lattices, the lines appear as multiplets. These multiplets spread out over a frequency range not wider than a few hundred kilocycles for the samples under discussion. Preliminary values for the frequencies, averaged over all lines in the multiplet ascribed to the Cl^{35} isotope, are given in Table I.

TABLE I.

Compound	Averaged frequency $\bar{\nu}(\text{Cl}^{35})$ Mc/sec	Number of lines in multiplet	Temperature
$\text{AlCl}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$	11.30	2	liquid air
SiCl_4	20.35	4	liquid air
SnCl_4	24.09	4	liquid air
$\text{SnCl}_4 \cdot \text{O}_2\text{NC}_2\text{H}_5$	23.08	6	liquid air
TiCl_4	6.05	4	liquid air
VOCl_3	11.54	2	liquid air
CrO_2Cl_2	15.68	2	liquid air
MoO_2Cl_2	15.40	1	room

The lines due to the Cl^{37} isotope have been observed to occur at the frequencies expected from the known ratio $Q[\text{Cl}^{37}]/Q[\text{Cl}^{35}] = 1.26878 \pm 0.00015$.²

* Now at Duke University, Durham, North Carolina.

¹ H. G. Dehmelt and H. Krueger, *Z. Physik* **129**, 401 (1951).

² R. Livingston, *Phys. Rev.* **82**, 289 (1951).

The Proton Magnetic Resonance Line in Liquid Crystals

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(Received December 1, 1952)

WE have observed the proton resonance in *para*-azoxyanisole both in the normal liquid and liquid crystal phase. The apparatus consisted of a twin- T bridge and the conventional associated components. The observations were made at a field of ~ 7300 gauss.

In the normal liquid state the line width is ≤ 0.1 gauss. As the temperature is reduced to below the transition point between the liquid and liquid crystal phase (135.8°C), the amplitude of the signal decreases greatly, and the line splits into three components as shown in Fig. 1. The separation between the two satellite peaks is

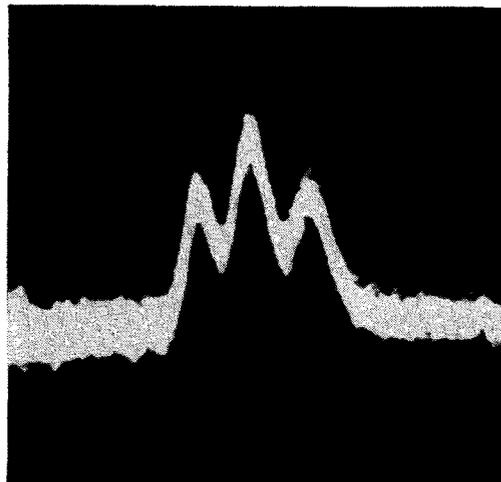


FIG. 1. Proton resonance signal from *para*-azoxyanisole in the liquid crystal phase.

about 3.3 gauss. As the temperature is decreased to below the transition point between the liquid crystal and crystalline phase (118°C) the signal again decreases, and we have been unable to obtain a satisfactory picture of the line shape.

The splitting in the liquid crystal phase may arise from a very strong hindering of the rotations of the methyl groups. An alternate possibility suggested by Dr. C. Kikuchi is that the protons in the benzene rings may be magnetically nonequivalent in the liquid crystal phase. We hope to extend these observations to the liquid crystal phases of *para*-azoxyphenetole and *para*-azoxyanisolephenetole.

Diffuse Spots of Pyrene at Higher Temperatures

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(Received December 17, 1952)

APYRENE crystal was obtained by slow evaporation from a benzene solution. The substance crystallizes in the monoclinic system with $a = 13.74\text{Å}$, $b = 9.22\text{Å}$, $c = 8.45\text{Å}$, and $\beta = 102^\circ 30'$. The space group of this crystal is



The number of molecules per unit cell is four. The crystal was mounted with the b axis vertical, and the x-ray beam was incident normally to $C(001)$ face of the crystal. The crystal shows extra Laue reflections from the $(\bar{3}10)$ and $(\bar{3}\bar{1}1)$ planes. These extra Laue reflections are found to be more intense as the temperature increases. At the temperature above 125°C, it was found that the lattice of the crystal is distorted.

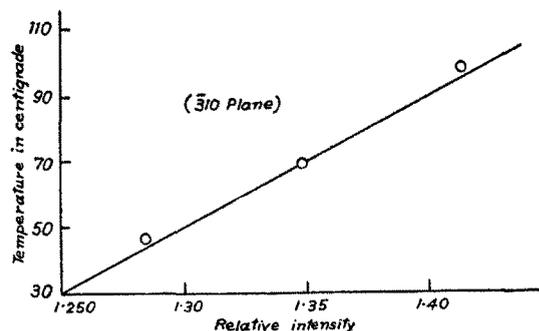


FIG. 1.

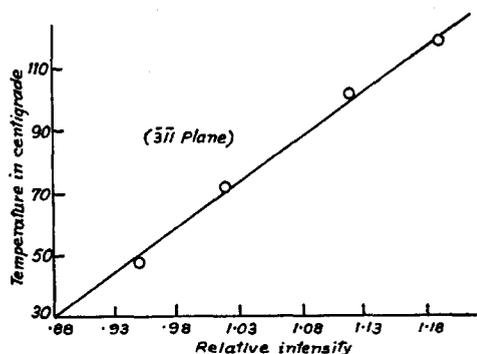


FIG. 2.

In order to have a standard for comparison of intensities of extra spots at different temperatures, a small quantity of aluminum powder was dusted over the crystal. The variation of the intensities of aluminum lines over the small range of temperature studied was neglected, however. The intensities were compared by means of a standard wedge, prepared according to the method of Robinson. The ratio of the (111) aluminum line to the maximum intensities of the extra spots were found by matching each of them against the standard wedge. It appears from the curve that intensities of extra spots increase very rapidly with the temperatures, and the variation of structure factor amplitude of two planes are different (see Figs. 1 and 2).

Erratum: Theory of Absorption Spectra of Carotenoids

[J. Chem. Phys. 20, 1661 (1952)]

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IN the previous letter¹ we attempted an explanation of the relation between absorption spectra and molecular lengths of carotenoids, making use of Tomonaga's method for electron gas with arbitrary couplings. We took into account the electron-spin for enumerating the number of electrons (occupying levels up to the Fermi maximum) only. If we take into account the spin degrees for wave functions we have, instead of Eq. (2) in the previous letter,¹ the following equation:

$$\delta = (L/\pi)^2(4/A)(N-2)^{-1}.$$

The empirical value of A thus becomes twice as large, $A = 709.5$. The rest needs no change.

¹ G. Araki and T. Murai, J. Chem. Phys. 20, 1661 (1952).

Addendum: Directed Valence as a Property of Determinant Wave Functions

[J. Chem. Phys. 17, 598 (1949)]

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AND

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IN his valuable recent review on "Quantum Theory, Theory of Molecular Structure and Valence" Professor Coulson¹ states that the idea of deriving directed valence properties from atomic wave functions (as written, for instance, under the form of determinants) "seems to have originated with Artmann,² but it has been "rediscovered" by Zimmerman and Van Rysselberghe³ . . ."

We wish to put on record that the tetrahedral valences of carbon were derived in this manner by one of us (P.V.R.) in 1933, that the calculations and results were communicated orally and by letter to several persons interested in the field, and that a communication

to the editor of the *Journal of the American Chemical Society* giving a condensed presentation of this fundamental point was not published for reasons which, coupled with other preoccupations, resulted in our abandoning further work of this type. The problem was resumed in 1946 and led to our submitting a paper³ to *The Journal of Chemical Physics* in July, 1948, publication following in July, 1949. In this paper we present the derivation of the tetrahedral valences of carbon in a manner identical with that of the intended communication of 1933, and we give reasons for offering our treatment of the whole problem of directed valences as an alternative to that of Artmann whose work had come to our attention through the abstract⁴ published in September, 1947.

¹ C. A. Coulson, Ann. Rev. Phys. Chem. 3, 1 (1952), see p. 8.

² K. Artmann, Z. Naturforsch. 1, 426 (1946).

³ H. K. Zimmerman, Jr., and P. Van Rysselberghe, J. Chem. Phys. 17, 598 (1949).

⁴ Chem. Abstracts 41, 5785 (1947).

The Dissociation Energy of Fluorine*

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RECENT spectroscopic data¹ on ClF imply a value for the dissociation energy of fluorine in the range 30–40 kcal/mol. Such a low dissociation energy would mean that considerable dissociation of diatomic fluorine into atoms must occur at relatively low temperatures. Doescher² and Wise³ have reported experimental results that indicate a value for $D_0(\text{F}_2)$ between 36 and 39 kcal/mol.

The experiments reported here were carried out in 1950 on a sample of fluorine obtained from the Pennsylvania Salt Manufacturing Company. The pressure exerted by this sample of fluorine, when contained in a closed system of copper which had been previously treated with fluorine, was measured as a function of temperature over the range 300–860°K with a Bourdon type Dura gauge in two runs on different days. Between the two runs a slight leak into the system occurred so that about six percent of the gas was air in the second run.

When corrections are made (1) for the presence of this air in the second run on the basis that it did not react and (2) for the cooler zones of the system, the pressure calculated on the basis of no dissociation of an ideal gas agreed at all temperatures below 800°K with the experimentally observed pressure with standard deviations of ± 0.02 inches of Hg for six points on the first day and of ± 0.03 for six points on the second day.

Three measurements at temperatures above 800°K showed differences between observed and calculated pressures considerably greater than any found for the twelve lower temperature measurements. If it is assumed that these differences are caused by the partial dissociation of F_2 into atoms, one may calculate at each temperature the degree of dissociation, the dissociation equilibrium constant, and, by using the available data for the free energy functions of F and F_2 ,⁴ the dissociation energy of F_2 . Because of the corrections necessary for different temperatures in different parts of the system, the degree of dissociation α and the equilibrium constant K are not simply related to the pressure difference.

The data and results are shown in Table I, in which the calculated and observed pressures in the second run have been corrected for the air leak. The uncertainties listed are obtained by assigning to each pressure an uncertainty of ± 0.03 inch of Hg.

TABLE I. Degree of dissociation, dissociation equilibrium constant, and dissociation energy of fluorine.

Run	T°K	P _{obs} (inches of Hg)	P _{calc} (inches of Hg)	α	K (10 ⁻³ atmos)	D ₀ (F ₂) (kcal)
1	815	1.48	1.40	0.07 ± 0.04	0.975 ± 1.10	33.4 ± 2.0
2	810	1.52	1.38	0.11 ± 0.05	2.49 ± 1.80	31.6 ± 1.6
2	860	1.72	1.46	0.21 ± 0.05	10.6 ± 5.4	31.2 ± 0.8