mental values. The calculations are quite sensitive to small variations in n^* and to a lesser extent to Z^*. It is quite possible also that the *form* of the Slater functions used are not suited to intensity calculation of Rydberg series members.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Intensity of Electronic Transitions of Methane and Carbon Tetrafluoride in the Vacuum Ultraviolet[1]

BY GEORGE MOE[2] AND A. B. F. DUNCAN

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The absolute intensities of some electronic transitions of methane and carbon tetrafluoride in the vacuum ultraviolet have been measured. *f*-numbers for these transitions were calculated and compared with experimental values. The nature of the transitions is discussed.

Introduction

Methane and carbon tetrafluoride are known from electron diffraction and infrared and Raman spectra to have tetrahedral structures.[3] The spectrum of methane in the vacuum ultraviolet region has been reported by Leifson,[4] Rose[5] and Duncan and Howe.[6] In an absorbing column of two meters at a pressure of 1.0 mm., the absorption was reported by Duncan and Howe to be continuous from about 1450 Å. to shorter wave lengths. Since this problem was begun, Wilkinson and Johnston[7] have reported some measurements of the absorption coefficients of methane, but their measurements were limited by the short wave length transmission of their apparatus and covered only the region from 1455 to 1370 Å. We have made measurements over the entire region extending from 1450 to 1100 Å. and have calculated an *f*-number for this transition using approximate wave functions.

The electronic spectrum of carbon tetrafluoride has not been reported previously. In the present work, we have obtained absorption coefficients from about 2000 Å. down to about 1330 Å. A broad transition with a maximum at 70,000 cm.$^{-1}$, and a weaker transition at 61,850 cm.$^{-1}$ were found. Additional transitions occur at shorter wave lengths for which absorption coefficients were not obtained. No analysis of the spectrum has been made yet, since the details have not been photographed. For the present work we are interested primarily in the broad transition occurring at 70,000 cm.$^{-1}$, for which we have obtained an integrated absorption coefficient and computed a theoretical *f*-number.

In the following section, experimental details for the measurements referred to above are given. Following this, some calculations which we have made of the *f*-numbers associated with the transitions in methane and carbon tetrafluoride are presented, along with a discussion of theoretical and experimental values.

Experimental Details and Results

Tank methane (Matheson Company, 99% pure) was liquefied with liquid nitrogen. The liquid was fractionated in vacuum, and only the middle third was retained. Before each use, a small sample from the storage bulb was fractionated again in the same way. The gas thus obtained showed no indication of impurities on our spectrograms.

Tank carbon tetrafluoride (Kinetic Chemical Company, about 95% purity) was treated in the same way as the methane. The chief impurity in the CF_4 was probably CF_3Cl. To determine whether the absorption could be partly due to CF_3Cl, spectrograms were taken with the sample cooled with freezing baths at temperatures of −80, −130 and −189°. Since CF_3Cl has a lower vapor pressure than CF_4, the partial pressure of CF_3Cl would be greater with increasing temperature if any were present. No difference was observed in the intensity of the absorption bands obtained at the three temperatures.

The apparatus and procedure for this study were the same as those used for the study of acetylene.[8] For preliminary studies on the absorption of carbon tetrafluoride, Eastman Kodak Company SWR film was used because of its high contrast. III-O ultraviolet sensitive plates were used for all spectrograms from which quantitative measurements were made.

Ten plates of methane covering the pressure range from 0.100 to 0.0025 mm. were taken. Most of the measurements were made on plates taken at the lower pressures. Absorption coefficients at wave lengths corresponding to more than 100 lines in the molecular hydrogen spectrum were obtained. These wave lengths were spaced throughout the absorption region of methane. Six plates of carbon tetrafluoride were taken at pressures ranging from 0.300 to 0.016 mm. At the lower pressure, the absorption is just strong enough to permit photometric measurements. Measurements of at about 100 lines between 1650 and 1330 Å. were made. Figure 1 shows the absorption coefficients plotted against wave number. The experimental *f*-numbers are reported in Table I. In the case of methane, there is some overlapping with the absorption

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(2) Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Raman spectra, CH_4: S. Bhagavantam, *Nature*, **130**, 740 (1932); C. M. Lewis and W. V. Houston, *Phys. Rev.*, **44**, 903 (1933). Infrared spectra, CH_4: J. P. Cooley, *Astrophys. J.*, **62**, 73 (1925); D. M. Dennison, *ibid.*, **62**, 84 (1925); *Rev. Modern Phys.*, **12**, 175 (1940). Raman spectra, CF_4: D. M. Yost, E. N. Lassettre and S. T. Gross, *J. Chem. Phys.*, **4**, 325 (1936). Infrared spectra, CF_4: A. Eucken and A. Bertram, *Z. physik. Chem.*, **B31**, 361 (1936); C. R. Bailey, J. B. Hall and J. W. Thompson, *Proc. Roy. Soc. (London)*, **167**, 555 (1938). Electron Diffraction, CF_4: H. Boersch, *Monatsh.*, **65**, 311 (1935).

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(5) A. Rose, *Z. Physik*, **81**, 758 (1933).

(6) A. B. F. Duncan and J. P. Howe, *J. Chem. Phys.*, **2**, 851 (1934).

(7) P. G. Wilkinson and H. L. Johnston, *ibid.*, **18**, 190 (1950).

(8) Preceding paper, THIS JOURNAL, **74**, 3136 (1952).

at shorter wave lengths and it was necessary to use an approximate method of resolution.[8] There was no appreciable overlapping in the case of CF_4.

TABLE I

EXPERIMENTAL f-VALUES, COEFFICIENTS AND RESULTS OF COMPUTATIONS OF f BY VARIOUS APPROXIMATIONS[a]

	CH_4($\nu_{max.}$ 82000 cm.$^{-1}$)	CF_4 ($\nu_{max.}$ 70000 cm.$^{-1}$)
f (exptl.)	0.342	0.0247
f (φ_1*)	.381(M)	.9023(M)
	.179(P)	.0286(P)
f $(3s)^0$	.1561(M)	.0127(M)
	.1084(P)	.0089(P)
f (3s)	.407(M)	.0433(M)
	.324(P)	.0480(P)
Coefficients		
a_2 (M)	.514	0.387
$b_2N_{2\sigma}$ (M)	.35	.407
a_1* (M)	1.585	.850
b_1*$N_{1\sigma}$ (M)	−0.638	− .494
a_2 (P)	.614	.567
$b_2N_{2\sigma}$ (P)	.291	.336
a_1* (P)	1.63	1.055
$b_1N_{1\sigma}$ (P)	−0.619	− .375
$N_{1\sigma} = {}^1/_2(1 + 3S_{\sigma_i\sigma_j})^{1/2}$	.368	.491
$N_{2\sigma} = {}^1/_2(1 - S_{\sigma_i\sigma_j})^{1/2}$	.590	.503

[a] The approximations differ only in the upper states concerned in the transitions. The upper states are indicated in parentheses following f. See text for explanation of (M) and (P).

A large error in the experimental results may arise because of unresolved rotational fine structure.[8] The highest resolution available at present is far from adequate to resolve this structure especially in carbon tetrafluoride. We conclude that lower limits of the integrated absorption coefficients have been measured, which may be much lower than the true values. It does not appear possible, however, to improve these experimental values significantly, because none of the factors which would indicate the presence of fine structure indirectly can be varied sufficiently in the present case. The path length cannot be varied. The pressure cannot be varied sufficiently because the spectrograph itself has to furnish the absorbing column at the short wave lengths of interest. The slit width could be varied, but if the absorption coefficient showed no change when this was done, the objection could be made that the slit width was always much wider than the line breadth.

Theoretical Calculations and Discussion

Non-localized molecular orbitals of a type CX_4 molecule may be obtained as follows[9]: Linear combinations of atomic orbitals, one from each of the four X atoms, are formed which transform in tetrahedral symmetry. These combinations are normalized and combined with atomic orbitals of carbon which have the same transformation properties. The *bonding* molecular orbitals of $CX\sigma$ are

$$\begin{aligned}\varphi_1(A_1) &= a_1(2s)_C + b_1N_{1\sigma}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)\\ \varphi_2(F_2) &= a_2(2p_x)_C + b_2N_{2\sigma}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4) \qquad (1)\\ \varphi_3(F_2) &= a_2(2p_y)_C + b_2N_{2\sigma}(-\sigma_1 + \sigma_2 - \sigma_3 + \sigma_4)\\ \varphi_4(F_2) &= a_2(2p_z)_C + b_2N_{2\sigma}(-\sigma_1 - \sigma_2 + \sigma_3 + \sigma_4)\end{aligned}$$

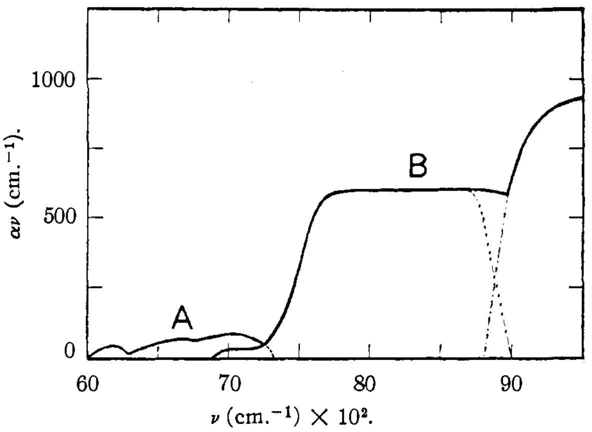

Fig. 1.—Absorption curves for CF_4 (A) and CH_4 (B).

In the case of CH_4, the σ_i are 1s atomic orbitals of H. In the case of CF_4, the σ_i are 2$p\sigma$ of fluorine. The axes are chosen so that the positive parts of the 2$p\sigma$ orbitals are directed toward the central carbon atom. The orbitals φ_2, φ_3, φ_4 have the same energy, which is certainly higher than φ_1.

The longest wave length transition in methane occurs from one of the former orbitals, or rather from a threefold degenerate (F_2) orbital. We assume that this is the case also in CF_4, and ignore the possibility that excitation occurs from a linear combination of non-bonding (2$p\pi$) electrons of the fluorines. This point will be considered briefly near the end of this paper.

The transition will occur to an unoccupied orbital which must have a symmetry (A_1). This orbital $\varphi_1^*(A_1)$ should be constructed to be orthogonal to φ_1. It will necessarily be orthogonal to the (F_2) orbitals. A proper form will be

$$\varphi_1^* = a_1^*(2s)_C + b_1N_{1\sigma}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

We treat provisionally the closed shell $(\varphi_3, \varphi_2, \varphi_4)^6$ with six electrons as three closed shells $(\varphi_2)^2$, $(\varphi_3)^2$, $(\varphi_4)^2$, and consider a transition in which only one of these closed shells is broken. The electron is excited to φ_1^*. We may write then

$$\begin{aligned}&Q_2(x) = (2)^{1/2}\int \varphi_2 x \varphi_1^* d\tau;\ Q_2(y) = 0 = Q_2(z)\\ &Q_3(y) = (2)^{1/2}\int \varphi_3 y \varphi_1^* d\tau;\ Q_3(y) = Q_2(x);\ Q_3(x) = Q_3(z) = 0\\ &Q_4(z) = (2)^{1/2}\int \varphi_4 z \varphi_1^* d\tau;\ Q_4(z) = Q_2(x);\ Q_4(x) = Q_4(y) = 0\end{aligned}$$

and

$$Q = \sqrt{Q_2^2 + Q_3^2 + Q_4^2} = (6)^{1/2}\int \varphi_2 x \varphi_1^* d\tau \qquad (2)$$

The coefficients in the functions φ_2 and φ_1^* must be known in order to evaluate Q in equation (2). This should be done by minimizing the total energy of the ground state with respect to a_1, b_1, a_2, and b_2. Then a_1^* and b_1^* could be found from a_1 and b_1 through orthogonality and normalization relations. This variational procedure may be subject to large errors, and it is a difficult problem. We attempted instead to estimate these coefficients from empirical electronegativities, following an approximate method of Mulliken,[10] using his equation (41). In our case the functions φ_1 and φ_2 were renormalized to give

$$\begin{aligned}a_1^2 + 2a_1b_1(4S_{(2s)(\sigma)})/2(1 + 3S_{\sigma_i\sigma_j}) + b_1^2 &= 1\\ a_2^2 + 2a_2b_2(4S_{(2p_x)(\sigma)})/2(1 - S_{\sigma_i\sigma_j}) + b_2^2 &= 1\end{aligned}$$

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[9] R. S. Mulliken, *J. Chem. Phys.*, 1, 492 (1933).

[10] R. S. Mulliken, *ibid.*, 3, 573 (1935).

The meaning of the overlap integrals S is clear from their subscripts. The charges ($-2e$) in the molecular orbitals were divided between C and H_4 (C and F_4) and the absolute values of a_1, b_1, a_2 and b_2 were obtained through the normalization conditions. We obtained two sets of coefficients. Those coefficients distinguished by (M) were obtained from the separate $(2s)_C$ and $(2p)_C$ electronegativities given by Mulliken.[11] The coefficients (P) were obtained from Pauling's[12] electronegativity values. Parallel computations have been made for both CH_4 and CF_4 using both sets of coefficients, in order to show in detail how the final f-values depend on the choice of coefficients.

The integral in equation (2) may now be written

$$\int \varphi_2 x \varphi_1^* \mathrm{d}\tau = a_2 a_1^* \int (2s)_C x (2p_x)_C \mathrm{d}\tau + 4a_2 b_1^* \int (2p_x)_C x\sigma \mathrm{d}\tau$$
$$+ 4a_1^* b_2 \int (2s)_C x\sigma \mathrm{d}\tau + 4b_1^* b_2 \int \sigma_i x \sigma_i \mathrm{d}\tau$$
$$+ 4b_1^* b_2 \int \sigma_i x \sigma_j \mathrm{d}\tau$$

In this expression, the sum of the last two integrals is $r(C - X) \cos \Theta(1 + S_{ij})$, with $r(C-H) = 1.093$ Å. and $r(C - F) = 1.36$ Å. Θ is one-half the tetrahedral angle and S_{ij} is the overlap integral between two H (or two F). The first single centered integral is easily evaluated. The second and third integrals

$$\int (2p_x)_C x\sigma \mathrm{d}\tau = Q_{p\sigma} \int (2s)_C\, x\sigma \mathrm{d}\tau = Q_{s\sigma}$$

were treated as follows.

For CH_4, in a coördinate system with origins at C and H, with the x-axis making an angle Θ' with the line r_C (the electron distance from C) and an angle Θ with the C–H bond line, then $x = r_C \cos \Theta'$ and $(2p_x) = N_{2px}\, r_C \cos \Theta' \exp(-Z_C r_C/2)$ and

$$Q_{p\sigma} = N_{2px} N_{1s(H)} \int r^2_C (\cos^2 \theta') \exp(-(Z_C r_C/2) - r_H)\, \mathrm{d}\tau$$

in atomic units. N is a normalizing factor. Expressing $(\cos^2 \Theta')$ in spherical harmonics, $\cos^2 \Theta' = 2P_2(\cos \Theta')/3 + {}^1/_3$. If use is made of the addition theorem of Legendre polynomials, with $(\Theta - \Theta') = \Theta_C$, the angle between r_C and the C–H line, it follows that

$$P_2(\cos \theta') = P_2(\cos \theta) \times P_2(\cos \theta_C) + (\text{other terms which will disappear on subsequent integration over } \varphi)$$

But $P_2(\cos \Theta)$ = zero, because Θ is one-half the tetrahedral angle and

$$Q_{p\sigma} = N_{2px} N_{1s}\, (3)^{-1} \int r^2_C \exp(-(Z_C r_C/2) - r_H) \mathrm{d}\tau$$

By a similar treatment

$$Q_{s\sigma} = N_{2s} N_{1s} \cos \theta \int r^2_C \cos \theta_C \exp(-(Z_C r_C/2) - r_H) \mathrm{d}\tau$$

The corresponding integrals for CF_4 contain an extra factor r_F and $\exp(-Z_F r_F/2)$ instead of $\exp(-r_H)$. These integrals were transformed to ellipsoidal coördinated and evaluated. Numerical values of these and other integrals are shown in Table II. The Slater values $Z_C = 3.25$ and $Z_F = 5.2$ were used.

Computed oscillator strengths based on Q from equation (2) are shown in Table I, with values of the coefficients used.

We considered also a possible transition from φ_2 to an atom like orbital involving a change in principal quantum number. This orbital is required to have a symmetry (A_1) and in addition it should be orthogonal to φ_1 and to φ_1^* as well. This latter condition is very difficult to satisfy, if at the same time φ_1^* is kept orthogonal to φ_1. After a number of trials with different forms of functions, it was found that a (3s) carbon function *with radial nodes*, constructed from ordinary (3s), (2s) and (1s) Slater functions with the requirement that they should be mutually orthogonal, was also very closely orthogonal to φ_1 (but not to φ_1^*). This function gave fair agreement with experiment for both molecules, as is shown in Table I.

TABLE II

NUMERICAL VALUES OF INTEGRALS

$\int (2p_x)_C \quad (3s)_C = 0.08954$ Å.
$\int (2p_x)_C \quad (2s)_C = .47006$ Å.
$\int (2p_x)_C \quad (1s)_C = .02124$ Å.
$\int (3s)_C \quad (1s)_H = .16435$ Å. (at r(C-H) = 1.093 Å.)
$\int (2s)_C \quad (1s)_H = .22822$ Å.
$\int (1s)_C \quad (1s)_H = .00228$ Å.
$\int (2p_x)_C \quad (1s)_H = .33173$ Å.
$\int (3s)_C \quad (2p\sigma)_F = .038626$ Å. (at r(C-F) = 1.36 Å.)
$\int (2s)_C \quad (2p\sigma)_F = .034885$ Å.
$\int (1s)_C \quad (2p\sigma)_F = .00100$ Å.
$\int (2p_x)_C \quad (2p\sigma)_F = .01042$ Å.

The normalized function $(3s)^0$ used was

$$(3s)^0 = 1.006(3s) - 0.188(2s) + 0.024(1s)$$

where (3s), (2s), (1s) are normalized Slater functions with Z = 1.45, 3.25 and 5.7 and n = 3, 2 and 1, respectively. These Z values were obtained by a direct application of Slater's rules and no variation of Z nor of n was studied. If a more general function, such as

$$\varphi = c(3s)_C + d(2s)_C + f(1s)_C + g(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

is tried, the coefficients cannot be determined by orthogonality with φ_1 and φ_1^* and normalization. If it is required merely that these component orbitals be mutually orthogonal, then the resulting f-values agreed very poorly with experiment, and are not listed in Table I.

Strangely enough, a Slater function (3s) with Z = 1.45 and n = 3 gave the best numerical agreement with experiment of any function of this type.

Finally we considered the possibility that the electron excited in CF_4 did not come from a bonding (C–F) orbital but from one of the molecular orbitals formed from the sixteen $2p\pi$ electrons of the four fluorines. We found only the orbitals which transformed like F_2 (and not those which transformed like F_1 and like E), and computed a dipole moment integral between one of the F_2 functions and an orthogonal F_2 function. The resulting f-number was of the order of 10^{-4}. There are obviously many other possibilities for excitation from orbitals of this nature. The energies of these orbitals relative to the bonding orbitals are completely unknown as well as their relative energy to each other, and it did not appear profitable to persue the matter further.

It is evident that the numerical results are sensitive to the choice of coefficients (for example the $f(\varphi_1^*)$ (M) value for CF_4 in Table I) and to this extent agreement with experiment is partly fortuitous. We do not believe that the agreement is

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(11) R. S. Mulliken, *ibid.*, **2**, 782 (1934).

(12) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 60.

completely accidental, particularly when results for the two molecules are compared. At the same time the moderately good agreement can be taken as an indication that the method of estimating coefficients in wave functions from electronegativities may be useful in crude intensity calculations.

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ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Further Studies of Nitrosyl Chloride as an Ionizing Solvent

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The ionization constant of $NOFeCl_4$ in liquid NOCl was determined from conductance data by the Shedlovsky method: $K_{\text{ion}} = 0.00373$ and $\Lambda_0 = 401.2$, at −10°. Its solubility is 93 g. $FeCl_3$ per 100 g. NOCl at 0°, and it forms the solid solvate $NOFeCl_4 \cdot NOCl$ (dissoc. pressure 224 mm. at 0°). The highly conducting $NOAlCl_4$ has a solubility of 61.2 g. $AlCl_3$ per 100 g. of NOCl at −25°, 68.6 g./100 at 0°, or 93 g./100 at 18°, and forms solid $NOAlCl_4 \cdot NOCl$ (dissoc. pressure 180 mm. at 0°). On the other hand, the nearly insoluble $NOBF_4$ and $(NO)_2SnCl_6$ are not recognizably solvated. Nitrosyl salts react with the slightly soluble $(CH_3)_4NCl$ in the sense of the acid–base neutralization $NO^+ + Cl^- \rightarrow NOCl$, as demonstrated by a conductometric titration of $NOFeCl_4$ by $(CH_3)_4NCl$ and by the partial neutralization equilibria of $NOBF_4$, $NOClO_4$ and $(NO)_2S_2O_7$, each with $(CH_3)_4NCl$. The idea that NO^+ represents acid, and Cl^- base, is further justified by the electrolysis of $NOFeCl_4$ in NOCl, forming NO at the cathode and Cl_2 at the anode. The transference ratio of NO^+ to $FeCl_4^-$ is about 7:1, suggesting a solvo-chain mechanism of transporting NO^+. In relation to this work, the vapor tensions of very pure NOCl were redetermined, with results near to the average of the most acceptable literature values. The dielectric constant was measured as 19.7 at −10°, 21.4 at -19.5° and 22.5 at −27°—a trend indicating a mild association, negatively correlated with temperature.

It was indicated earlier that certain nitrosyl salts of complex anions are very soluble strong electrolytes in liquid nitrosyl chloride, while others are relatively insoluble or poorly conducting.[2] The study now has been extended to establish a more definitely quantitative understanding of NOCl as an ionizing solvent, and to develop the increased variety of chemical knowledge implied by solvation, the phenomena accompanying electrolysis, and reactions of the neutralization type.

Experiments, Results and Interpretations

I. Properties of Nitrosyl Chloride

Purification.—Nitrosyl chloride, prepared by the action of hydrogen chloride upon nitrosyl acid sulfate,[3] was purified first by a rough fractional condensation and then by a helix-packed fractionating column, attached to the high-vacuum apparatus and operating with a reflux temperature of −42° (boiling propane), in a fairly dark room. In the final refractionation, one-third of the product was rejected as first and last fractions, which still showed vapor tension agreement. The samples were preserved in sealed tubes at −78°, in a dark cupboard to minimize photodecomposition, and usually were repurified between experiments.

Vapor Tensions.—The vapor tensions of several different samples of purified nitrosyl chloride were measured over the range −48 to −6°, in a black painted apparatus employing a quartz Jackson-type gage[4] as a null-instrument. The ammonia and sulfur dioxide vapor tension thermometers,[5] and a standardized mercury thermometer graduated to 0.1°, were used in their appropriate ranges. The results, presented in Table I, determine the equation $\log_{10} p_{\text{mm.}} = -(1373.82/T) + 1.75 \log_{10} T - 0.0036716T + 4.74582$, from which the check values were calculated (average deviation 0.05 mm.). This implies the normal boiling point to be −5.38°, or near the average of previous determinations.[6-9] Taking the critical pressure as 92 atm.,[10] the heat of vaporization is calculated as 5953 cal./mole. at the boiling point, and the Trouton constant is 22.23 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF PURE NITROSYL CHLORIDE

t, °C.	−47.59	−46.39	−44.37	−41.97	−31.77	−29.38
$p_{\text{mm.}}$ (obsd.)	88.11	94.97	107.29	123.36	217.79	246.82
$p_{\text{mm.}}$ (calcd.)	88.19	94.90	107.18	123.47	217.77	246.90
t	−25.63	−22.27	−17.52	−15.03	−9.23	−7.79
p (obsd.)	299.05	353.10	443.13	497.28	644.34	685.85
p (calcd.)	299.03	353.14	443.11	497.27	644.37	685.85

The Dielectric Constant.—The only previous value of the dielectric constant of nitrosyl chloride, 18.2 at 12°, was obtained by extrapolation from solutions of NOCl in CCl_4.[11] Direct determinations now have been made at three lower temperatures, using an 18-ml. cell in which the pure liquid covered two parallel platinum plates 6 cm. in diameter, rigidly held 1 mm. apart. Capacitances were measured by a Schering bridge circuit (Capacitance Bridge Type 716-C, General Radio Co.), employing a Hewlett-Packard Model 200A variable oscillator as a source. The detector circuit consisted of a one-stage amplifier and oscilloscope, connected to the bridge in the manner recommended by Jones, Mysels and Juda.[12] The cell and connecting wires were surrounded by grounded shields. The temperature of the bath (trichloroethylene contained in an unsilvered dewar vessel sur-

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[1] This paper represents a dissertation presented by Donald E. McKenzie to the Graduate Faculty of the University of Southern California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1950. The support of a considerable part of this work through a research fellowship granted by the Standard Oil Company of California is gratefully acknowledged. The present address of Dr. McKenzie is Canadian National Research Council, Chalk River, Ontario, Canada.

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