

***l*-1,8-Bis-(2'-hydroxy-3'-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) *d*-Antimonyl Tartrate Pentahydrate.**—The *dl*-iodide described above was suspended in water (150 ml.) and excess freshly precipitated silver chloride added. The mixture was then warmed to 50° and vigorously shaken for 20 minutes, after which the solids were filtered off and washed. The combined filtrate and washings (total volume 200 ml.) were then slowly treated with an almost saturated solution of potassium *d*-antimonyl tartrate (2.23 g.) in hot water, the sides of the container being scratched during the addition. Crystalline black prisms separated. These were collected and recrystallized several times from hot water to which a little potassium *d*-antimonyl tartrate was added. The final crystalline product charred on heating.

*Anal.* Calcd. for  $\text{Co}(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2)(\text{C}_4\text{H}_7\text{O}_7\text{Sb}) \cdot 5\text{H}_2\text{O}$ : Co, 6.7; Sb, 13.8; H<sub>2</sub>O, 10.2. Found: Co, 6.7; Sb, 13.7; H<sub>2</sub>O, 10.3.

A 0.02% solution in water gave  $\alpha_D - 0.94^\circ$  in a 1-dm. tube, whence  $[\alpha]^{20D} - 4,700^\circ$ .

***l*-1,8-Bis-(2'-hydroxy-3'-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) Iodide Dihydrate.**—The *l*-complex *d*-antimonyl tartrate just described was suspended in water (2.5 g. in 100 ml.) at 40° and hydrochloric acid (5 *N*, 10 ml.) added. The mixture was then vigorously shaken until all the antimony had been precipitated as antimony oxy-

chloride. After filtration, the green-brown solution of the active chloride was treated with potassium iodide. The precipitated active iodide was collected and recrystallized twice from hot water and obtained in black needles which sintered at 207° and melted at 212°.

*Anal.* Calcd. for  $\text{Co}(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2) \cdot 2\text{HI} \cdot \text{O}$ : Co, 8.8; I, 19.0. Found: Co, 8.8; I, 19.1.

A 0.02% aqueous solution gave  $\alpha_D - 1.10^\circ$  in a 1-dm. tube at 20°, whence,  $[\alpha]^{20D} - 5,500^\circ$  and  $[M]^{20D} - 36,700^\circ$ .

***d*-1,8-Bis-(2'-hydroxy-3'-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) Iodide Dihydrate.**—The filtrate left after precipitation of the *l*-complex *d*-antimonyl tartrate was strongly dextrorotatory (*vide supra*). It was precipitated fractionally with potassium iodide. The first (least soluble) fractions were mainly composed of *dl*-complex iodide. The more soluble fractions were rich in the *d*-complex iodide. They were collected and recrystallized many times from hot water to which potassium iodide was added until the specific rotation was constant. The black needles sintered at 207° and melted at 212°.

*Anal.* Found: Co, 8.9; I, 19.1.

A 0.02% aqueous solution gave  $\alpha_D + 1.10^\circ$  in a 1-dm. tube at 20° whence,  $[\alpha]^{20D} + 5,500^\circ$  and  $[M]^{20D} + 36,700^\circ$ .

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## Intensities of Electronic Transitions of Acetylene in the Vacuum Ultraviolet<sup>1</sup>

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The absolute intensities of thirteen separate electronic transitions of acetylene in the region 1520–1050 Å. have been measured quantitatively. A one-meter vacuum grating spectrograph was used to photograph the spectrum. Molecular hydrogen lines occurring in this region from a low pressure hydrogen discharge tube were used as background for the absorption. Absorption coefficients were determined at wave lengths where these lines occurred, using the methods of photographic photometry. "Oscillator strengths" (*f*-numbers) for the transitions were found. The values obtained are compared with theoretical *f*-numbers calculated from approximate wave functions.

### Introduction

The ultraviolet spectrum of acetylene has been the subject of numerous investigations. Early studies were confined to the region above 1800 Å. where some complex band systems were found between 2400 and 2000 Å.<sup>3</sup> The work was extended to the far ultraviolet by Price<sup>4</sup> and Price and Walsh.<sup>5</sup> The absorption between 2400 and 1500 Å. consists of many weak diffuse bands, the analysis of which is as yet unsatisfactory. From 1500 to 1050 Å., intense absorption bands representing fifteen electronic transitions were reported by Price,<sup>4</sup> who assigned the transitions to two Rydberg series. These series converge to the same ionization limit at about 92,000 cm.<sup>-1</sup>.

The present investigation is directed primarily to the measurement of the intensities of these Rydberg series members. It was not possible with the equipment available to include the transitions at longer wave lengths in this work. Hence, only

transitions between 1520 and 1050 Å. will be considered. The general theory of calculation of intensities of electronic transitions is discussed in detail in the report by Mulliken and Rieke.<sup>6</sup> The vector *Q* is

$$Q = \int \psi_k \sum_i r_i \psi_l d\tau \quad (1)$$

$\psi_k$  and  $\psi_l$  are the wave functions for the normal and excited electronic states, respectively.  $r_i$  is the radius vector of the *i*<sup>th</sup> electron which enters into the transition. Transitions are either of the perpendicular type or the parallel type. In the former the electric moment moves perpendicular to the internuclear axis, which may be chosen to lie in the *z* direction. *r* then becomes either *x* or *y*. For parallel type transitions,  $r = z$ .

Theoretical *Q*<sup>2</sup>'s are compared with experimental *f*-numbers which are obtained in the following way. The absorption coefficient,  $\alpha_\nu$ , is determined at a large number of wave lengths within the absorption band.  $\alpha_\nu$  is defined by the equation

$$I_\nu/I_\nu^0 = e^{-\alpha_\nu l_0} \quad (2)$$

where  $I_\nu/I_\nu^0$  is the fraction of light of frequency  $\nu$  (cm.<sup>-1</sup>), transmitted by a column of gas of length  $l_0$ , measured in cm. at 0° and 76 cm. pressure. To obtain the total absorption strength for an entire electronic transition,  $\alpha_\nu$  is integrated over the

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(2) Part of 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) (a) S. C. Woo, T. K. Liu, T. C. Chu and W. Chih, *J. Chem. Phys.*, **6**, 240 (1938); (b) G. B. Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931); (c) G. Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

(4) W. C. Price, *Phys. Rev.*, **45**, 843 (1934); **47**, 444 (1935).

(5) W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

(6) R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

whole range of  $\nu$ 's belonging to the transition. Theoretical values of  $Q^2$  (in  $\text{cm.}^2$ ) are related to theoretical  $f$ -numbers by the approximate equation<sup>6</sup>

$$f = 1.085 \times 10^{11} \nu Q^2 \quad (3)$$

where  $\nu$  is the frequency at maximum of the experimental absorption curve.

The following section is concerned with the details of the method for obtaining experimental  $f$ -numbers, along with a description of the apparatus used. Following this the results of some theoretical calculations of  $f$ -numbers from  $Q^2$  values are presented and compared with experiment.

### Experimental Details

Commercial tank acetylene was purified according to the method described by Conn, Kistiakowsky and Smith.<sup>7</sup> This treatment removes acetone which is used as a solvent in tank acetylene, as well as traces of oxidizing and reducing agents which might be present. The gas was dried by passing through towers of  $\text{CaCl}_2$  and Dehydrite, and stored in a 5-liter flask. Before each use the acetylene was repeatedly frozen down with liquid  $\text{N}_2$  and outgassed in vacuum.

The spectrum was photographed in a vacuum grating spectrograph similar in essential design to one described by Sawyer.<sup>8</sup> The grating had a radius of curvature of about one meter, and was ruled on aluminum with 30,000 lines to the inch. The theoretical resolving power in the first order was about 40,000, and the dispersion about  $8.32 \text{ \AA./mm.}$  The grating was mounted at about normal incidence a first order spectra from 0 to  $2400 \text{ \AA.}$  could be photographed in one setting. The slit height was 2 mm., and the width was usually 0.06 mm. Some difficulty was experienced in bending glass photographic plates 0.8 mm. thick to the required curvature; breakage was minimized by coating the backs of the plates with gelatin. The spectrograph had a volume of about 70 liters and could be evacuated to a pressure of  $1 \times 10^{-6} \text{ mm.}$  The pressure rise was less than 0.001 mm. in 24 hours.

A glass hydrogen discharge tube of conventional design, operated on direct current, was used as a light source. Currents from 20 to 50 ma. were used. The operating voltage was about 1800 volts. This source gives numerous well resolved lines of known wave length<sup>9</sup> at which  $\alpha_\nu$  may be measured. A shutter cut off light from the spectrograph except during exposures. Line voltage fluctuations were reduced by insertion of a constant voltage transformer in the primary circuit.

The intensity of the discharge depends rather critically on the pressure of  $\text{H}_2$ . Our experimental conditions were complicated by the use of the slit to separate the acetylene, at a constant pressure in the spectrograph, from the  $\text{H}_2$  at a higher pressure in the discharge outside. Hydrogen was pumped through the discharge tube continuously at a pressure which was not quite constant, since a little flowed into the spectrograph through the slit. This caused small changes in the intensity of the source, which were seen in the recorded output of a photocell exposed to visible light from the source. Independent measurements showed that the intensity of vacuum ultraviolet radiation was directly proportional to the intensity of visible radiation, and compensation for this intensity variation was made by adjustment of the voltage on the discharge tube with a Varitran.

After the spectrograph had been evacuated to a pressure of less than  $10^{-6} \text{ mm.}$  a sample of acetylene was then frozen down and repeatedly outgassed. The desired amount was admitted into a calibrated volume and the pressure measured accurately. The hydrogen discharge tube was then turned on and allowed to run for 20–25 minutes with the shutter closed. Next, five or six exposures of the source were taken at constant intensity for varying lengths of time for plate calibration. An exposure then was made with acetylene at

a definite pressure, for a time equal to the longest calibration exposure. The spectrograph was isolated from the main pumping system during actual exposure intervals. Between the calibration exposures, the  $\text{H}_2$  which had diffused into the system was pumped out.

Eastman Kodak Company III-0 ultraviolet sensitive photographic plates were used for this work. After exposure the plates were bathed for two minutes in dry ethylene dichloride and dried for two minutes. They were then developed in fresh Eastman developer D-19 for exactly five minutes at  $18^\circ$  in a tray which was continuously agitated with a rocking motion. After fixing and washing, the gelatin backing was removed by scraping before allowing the plates to dry.

Microphotometer tracings were made of all the calibration exposures as well as the exposures through acetylene on the same plate.

The absorption coefficients,  $\alpha_\nu$ , at the frequency of  $\text{H}_2$  band lines were obtained in the following manner, using Eq. 2. The photographic densities,  $D$ , were obtained from the microphotometer traces in the usual way,<sup>10</sup> and plotted against the logarithm of the exposure time in minutes. This served as the calibration curve for the line at this wave length. Then  $D$  was obtained for the exposure through the absorbing gas, and the corresponding time,  $t$ , read off from the calibration curve. The actual exposure time was  $t_0$ . The quantity  $\log_e t_0/t = \log_e I_0/I$  is equal to  $\alpha_\nu t_0$ , assuming no reciprocity law failure. Actually at the times and intensity used this contributes a 4–5% error (from data on the emulsions used) and  $\alpha_\nu$  could have been increased by a factor 1.05 to allow for this. The experimental  $f$  values would have increased by about the same factor.

The absorption coefficients thus measured were plotted against the frequency in  $\text{cm.}^{-1}$ . In most cases the  $\text{H}_2$  lines occurred at closely spaced intervals so that the shape of the band envelopes could be found unambiguously. In one or two cases where the  $\text{H}_2$  lines are more widely spaced, the position of the band center could not be determined accurately in this way, and the wave length of the center was taken from the data of Price. The complete absorption curve thus obtained is shown in Fig. 1. The analysis of Price<sup>4</sup> was used in assignment of vibrational bands to electronic transitions. The area under the curve corresponding

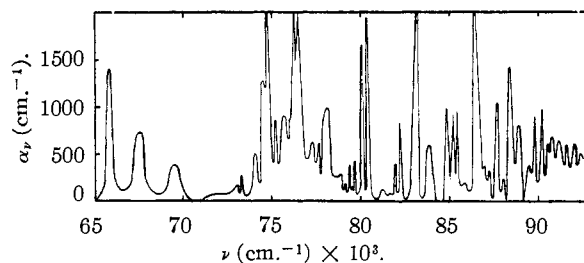


Fig. 1.—Absorption curve of acetylene.

to each electronic transition was measured with a precision planimeter. This gave the  $\int \alpha_\nu d\nu$  for each transition. The  $f$ -numbers were obtained from the areas using the relation

$$f = 4.20 \times 10^{-8} \int \alpha_\nu d\nu \quad (4)$$

The photometric technique is subject to the usual errors of photographic photometry. These are discussed in detail in a number of references on the subject.<sup>10,11</sup> In addition to the errors of photometry one must also consider the effect of slit width on the measurement of line intensity. In the case of truly continuous spectra this effect is negligible since the absorption coefficient does not change appreciably over the range of frequencies covered by the width of the spectral line. In the present case some vibrational structure was partly resolved but no structure was present which was at all comparable to the slit width. The slit width used throughout our investigation was 0.060 mm., corresponding to a range of about  $0.5 \text{ \AA.}$  on the plate. At 1500

(7) J. B. Conn, C. B. Kistiakowsky and E. A. Smith, *THIS JOURNAL*, **61**, 1868 (1939).

(8) R. A. Sawyer, *J. Opt. Soc. Am. and Rev. Sci. Instr.*, **15**, 303 (1927).

(9) (a) T. Lyman, *Astrophys. J.*, **23**, 181 (1926); (b) T. Hori, *Z. Physik*, **44**, 838 (1927); (c) C. R. Jeppesen, *Phys. Rev.*, **44**, 165 (1933).

(10) R. A. Sawyer, "Experimental Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1944, p. 284.

(11) (a) W. E. Forsythe, editor, "Measurement of Radiant Energy," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 326; (b) G. R. Harrison, R. C. Lord and J. R. Loofbourov, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 309.

Å., this corresponds to about 22 cm.<sup>-1</sup>. The narrowest band appearing in the spectra which we photographed for this work was about 150 cm.<sup>-1</sup> wide, and it was possible to make four measurements of  $\alpha_\nu$  over the width of this band.

We estimate that the errors arising from photometric techniques in the present work is between 5 and 10%, as has been found in previous work in this Laboratory and by others. Reciprocity law failure is estimated to contribute an additional 5%, and we conclude that the maximum error in the experimental absorption coefficients is about 15%.

It may be asked, however, if the spectrum being measured is in reality composed of numerous narrow rotational lines which are not resolved under our experimental conditions, which cause extreme variations of  $\alpha_\nu$  over a slit width of about 20 cm.<sup>-1</sup>. Price<sup>4</sup> photographed these bands with a higher resolving power and dispersion than we had available, and described the bands near 1500 Å., on which we have made intensity measurements as "very diffuse." He interpreted this diffuseness on the basis of predissociation caused by interaction of the excited level with the normal level of the molecule. We have assumed, largely on the basis of this observation, that  $\alpha_\nu$  is essentially constant over a slit width corresponding to each of the background lines. Price pointed out, however, that his dispersion was inadequate to resolve the rotational structure, if present.

Some evidence for absence of extreme variation of  $\alpha_\nu$  across a slit width is found in a study of the transmission,  $\log_e (I_0/I)$ , for individual lines, as a function of pressure of the absorbing gas. It was found that the transmission depended linearly on the pressure for many lines, some of which were near the tails of vibrational bands, where departures from Lambert's law might be expected to be largest. Unfortunately the pressure variation may have been too small (from 0.015 to 0.06 mm.) in these cases, and the absolute pressure too low to cause any additional broadening. Consequently this evidence is not conclusive.

Perhaps it is best to conclude that *minimum* values of the integrated absorption coefficients have been obtained, but that the true values may be much larger.

### Experimental Results

Table I shows the experimental results which are based on eleven plates of acetylene at pressures ranging from 0.0026 to 0.55 mm. In Table I  $n$  is the principal quantum number, and  $\nu_{\max}$  is the frequency of the maximum of the absorption band in cm.<sup>-1</sup>. The series members with  $n = 3, 4, 5$  and 6 do not overlap, and hence offer no problem of resolution. In the higher members of the series, there is considerable overlapping of the bands and the amount of the band envelope to be assigned to each transition must be estimated. In cases

TABLE I  
EXPERIMENTAL AND CALCULATED  $f$ -NUMBERS FOR ACETYLENE

| $n$ | $\nu_{\max}$ | $f$          |                   |
|-----|--------------|--------------|-------------------|
|     |              | $f$ (exptl.) | $f$ (calcd.)      |
|     |              | Series I     | ( $nd \pi g$ )    |
| 3   | 74516        | 0.173        | 0.07              |
| 4   | 83140        | .0427        | .01               |
| 5   | 86665        | .0259        | .00006            |
| 6   | 88431        | .0165        |                   |
| 7   | 89464        | .0049        |                   |
| 8   | ...          | ....         |                   |
| 9   | 90560        | .0060        |                   |
|     |              | Series II    | ( $nd \delta g$ ) |
| 3   | 65790        | 0.0616       | 0.20              |
| 4   | 80116        | .0477        | .01               |
| 5   | 85226        | .0247        | .0002             |
| 6   | 87636        | .0111        |                   |
| 7   | 88946        | .0156        |                   |
| 8   | 89743        | .0119        |                   |
| 9   | 90260        | .0085        |                   |

where overlapping was not too large, this was done by dividing the ordinate at the minimum between two overlapping transitions by two and extrapolating the curve from the two peaks through this point to the base of the curve. In this way  $f$ -numbers for the series members with  $n = 7, 8$  and 9 were estimated. The accuracy of the results for these members is therefore not expected to be as good as those obtained for the non-overlapping bands.

It is noted from Table I that in series I there is a rapid decrease in intensity in going from  $n = 3$  to  $n = 4$ . The decrease is not so rapid, and is fairly uniform, in going to the higher members. In series II, there is only a gradual decrease throughout. Except for the  $n = 3$  members of the two series, which differ appreciably, the corresponding members of the two series have about equal  $f$ -numbers. These results will be compared with some theoretical calculations in the section following. The calculated  $f$ -numbers are included in Table I for reference in making these comparisons.

### Theoretical Calculations and Comparison with Experiments

The electronic configuration of acetylene in its normal state may be formulated in many ways. A partly localized molecular orbital formulation is

$$(\sigma_{CAHA})^2 (\sigma_{CBHB})^2 (\sigma_{2di})^2 (\pi_{u,2p})^4 \quad (5)$$

where the two electrons in  $(\sigma_{CAHA})$  are from carbon atom C and its attached H, with similar meaning for  $(\sigma_{CBHB})$ . The orbital  $(\sigma_{2di})$  is a linear combination

$$(\sigma_{2di}) \sim (2d_{iCA}) + 2d_{iCB}$$

where

$$(2d_{iCA}) \sim (2s_{CA} + 2p\sigma_{CA})$$

There appears to be little doubt that the orbital  $\pi_u$  has the highest energy of all orbitals occupied in the normal state; the transitions corresponding to the longest wave length absorption spectra would then arise from excitation of an electron from this orbital. It is expected that the transition of *lowest* energy will occur when the electron is excited to an anti-bonding orbital,  $\pi_g$ . It has been suggested that the transition occurring at 2400–2200 Å. in acetylene may be of this type.<sup>12</sup> At shorter wave lengths there may be transitions to other upper states associated with  $\pi_u \rightarrow \pi_g$ . There will be also some transitions to Rydberg orbitals. We have made some theoretical calculations of the dipole moment integrals, and hence intensities, associated with transitions of the Rydberg type, using approximate wave functions. The complete electronic wave function will be a product of orbital functions of the 14 electrons, corresponding to configuration (5). However, it has been shown that the dipole moment integral calculated from the complete wave functions is the same as that calculated by ignoring electrons which remain in closed shells during the transition.<sup>13</sup> The closed shell  $(\pi_u, 2p)^4$  of equation (5) may be reformulated  $(\pi_u)_1^2 (\pi_u)_{11}^2$ . Tentatively we consider that the excitation occurs from  $(\pi_u)_1^2$ , and the shell  $(\pi_u)_{11}^2$  remains closed. We use  $\psi_k = \pi_u (1) \pi_u (2)$  for the

(12) R. S. Mulliken, *J. Chem. Phys.*, **3**, 526 (1935).

(13) R. S. Mulliken, *ibid.*, **8**, 234 (1940).

normal state function and  $\psi_1 = (2)^{-1/2}[\pi_u(1)R(2) + \pi_u(2)R(1)]$  for the excited state function, where  $R$  is a Rydberg orbital as yet unspecified, and (1) and (2) refer to the two electrons.

These functions are inserted into Eq. (1), and the two-electron integrals are reduced to one-electron integrals, making use of the fact that  $\pi_u$  is orthogonal to  $R$  and both  $R$  and  $\pi_u$  are taken as normalized. The result of the reduction is

$$Q_1 = (2)^{1/2} \int \pi_u r R d\tau$$

An identical expression is obtained for excitation from the shell  $(\pi_u)_1^2$  and since  $Q^2 = Q_1^2 + Q_2^2$ , the total dipole moment integral

$$Q = 2 \int \pi_u r R d\tau \quad (6)$$

$(\pi_u)$  was approximated by a linear combination of normalized  $2p_x$  atomic wave functions, *i.e.*

$$\pi_u = (2p_x(C_A) + 2p_x(C_B))/(2 + 2S_{\pi\pi})^{1/2} \quad (7)$$

where  $S_{\pi\pi} = \int 2p_x(C_A) 2p_x(C_B) d\tau$  is the overlap integral for the atomic orbitals  $2p_x(C_A)$  and  $2p_x(C_B)$ . Substituting (7) into (6)

$$Q = 4(2 + 2S_{\pi\pi})^{-1/2} \int (2p_x)r(R) d\tau \quad (8)$$

The form of the Rydberg orbital will now be considered. This will be similar in nature to an atomic function of a united atom. Possibilities to be considered are  $ns\sigma_g$ ,  $nd\sigma_g$ ,  $nd\pi_g$  and  $nd\delta_g$ . We accept the conclusions of Price<sup>4</sup> that his series I bands are of a parallel type ( $r = z$ ), and series II bands are of a perpendicular type ( $r = x$  or  $y$ ). Then  $Q$  for series I will be zero unless  $R$  in Eq. (8) is  $nd\pi_g$ . There are several possibilities for series II, since  $Q$  vanishes only for  $R = nd\pi_g$ . The possibilities are  $ns\sigma_g$ ,  $nd\sigma_g$  and  $nd\delta_g$ . Reference to the usual correlation diagrams shows that  $ns\sigma_g$  corresponds to the bonding molecular orbital  $\sigma_g(n-1)p$  which may be approximated by  $[(n-1)p\sigma + (n-1)p\sigma]$  at least for  $n = 3, 4$ . Similarly  $3d\sigma$  corresponds to a bonding molecular orbital  $3s$  which may be approximately  $(3s + 3s)$ . Also for series I,  $3d\pi_g$  may be approximated by the antibonding molecular orbital  $\pi_g 2p$  of the approximate form  $(2p\pi - 2p\pi)$ . In the latter approximation the  $f$  value obtained ( $> 1$ ) was far higher than anything observed experimentally.

In order to evaluate equation (8), with  $R = nd\pi_g$  for series I and  $R = nd\delta_g$  or  $nd\sigma_g$  for series II, the analytical forms of these orbitals must be specified.  $nd\pi_g$  is the atomic function  $nd_{xz}$  or  $nd_{yz}$  and  $nd\delta_g$  is  $nd_{x^2-y^2}$  or  $nd_{xy}$ , and  $nd\sigma$  is  $nd_{z^2}$ . Calculations for transitions to  $ns\sigma_g$  have not been made. We have then for series I

$$\begin{aligned} Q(\text{series I}) &= C \int (2p_x) z nd_{yz} d\tau \\ &= C \int (2p_x) z nd_{xz} d\tau \quad (9) \\ &\text{with } C = 4(2 + 2S_{\pi\pi})^{-1/2} \end{aligned}$$

and for series II

$$\begin{aligned} Q_x &= C \int 2p_x x nd_{x^2-y^2} \\ &= C \int 2p_x x nd_{xy} \\ &= C \int 2p_x x nd_{z^2} \cong 0.577 C \int 2p_x x nd_{x^2-y^2} \\ Q_y &= C \int 2p_x y nd_{xy} \\ &= C \int 2p_x y nd_{z^2} = 0.577 C \int 2p_x x nd_{y^2-z^2} \end{aligned} \quad (10)$$

and since  $Q_x = Q_y = Q$

$$\begin{aligned} Q(\text{series II, } nd\delta_g) &= C \int 2p_x x nd_{x^2-y^2} \\ Q(\text{series II, } nd\sigma_g) &\cong 0.577 C \int 2p_x x nd_{z^2-y^2} \end{aligned}$$

The integral of equation (8) was evaluated in elliptical coordinates, with the  $2p_x$  function centered on one of the carbons and the  $(nd)$  function referred to a center midway between the two nuclei, which are located on an axis extending in the  $z$  direction. The equilibrium C-C distance is taken as 1.2074 Å.<sup>14</sup>  $S_{\pi\pi}$  was obtained from tables of overlap integrals.<sup>15</sup>

Analytical forms of the functions used were of the Slater type<sup>16</sup>

$$N r^{n^* - 1} \exp(-hr) Y(l, m | \theta, \varphi)$$

where  $N$  is a normalizing factor,  $n^*$  the "effective principal quantum number,"  $Y(l, m | \theta, \varphi)$  a normalized spherical harmonic, and  $h$  represents  $Z^*/n^*a_0$ .  $Z^*$  is given by  $(Z - s)$ , where  $Z$  is the nuclear charge and  $s$  is the "screening constant."  $a_0$  is the Bohr radius.

The detailed forms of  $Q$  for the two series, after integrating over the angle  $\varphi$ , are

$$Q(\text{Series I}) = CN_e N_u \int r r_{e'u}^{(n^* - 1)} \exp(-h_e r_e - h_u r_u) z \sin \theta_e \sin \theta_u \cos \theta_u d\tau \quad (9a)$$

$$\begin{aligned} Q(\text{Series II}) &= (2)^{1/2} CN_e N_u \int r r_{e'u}^{(n^* - 1)} \exp(-h_e r_e - h_u r_u) x \sin \theta_e \sin^2 \theta_u d\tau \quad (10a) \\ &= 1.733 Q(nd\sigma_g) \end{aligned}$$

where the subscript  $u$  refers to the united atom orbital.  $h_e$  in the above equation is given by Slater's rules as  $3.25/2a_0$ , since  $n^* = n = 2$ . Choices of  $Z^*$  and of  $n^*$  for the united atom orbitals are much more difficult.  $Z^*$  should actually be equal to one for the higher members of the series and we have used  $Z^* = 1$  for all values of  $n$ . For  $n^*$  we used values determined from the Rydberg series formulas given by Price,<sup>4</sup> with  $n^* = 2.5, 3.5$ , etc., for series I and  $n^* = 2.05, 3.05$ , etc., for series II. However, the integrals in equation (9a) and (10a) cannot be evaluated in elliptical coordinates for values of  $n^*$  which are not integers. The integrals were evaluated for  $n^* = 2, 3, 4$ . For  $n^* > 4$  it is sufficiently accurate to evaluate the integrals in a spherical polar coordinate system, since the average distance of the electron from either center is very large in comparison with the distance between centers. Values for  $n^* = 5$  for the two series were obtained in this way. Results at the desired values of  $n^*$  were obtained by graphical interpolation.  $f$ -numbers corresponding to  $Q$  values calculated in this way are reported in Table I. Values for series II ( $nd\sigma_g$ ) are not given but are approximately one-third<sup>17</sup> the values for ( $nd\delta_g$ ).

It is evident that the calculations are in very bad agreement with the experimental values for members of both series with  $n \geq 5$  and in fact calculations for even the first two members are not very good, but possibly are acceptable for order of magnitude.

It is evident also that the calculated values decrease much more rapidly with  $n$  than the experi-

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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<sup>1</sup>

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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.<sup>3</sup> The spectrum of methane in the vacuum ultraviolet region has been reported by Leifson,<sup>4</sup> Rose<sup>5</sup> and Duncan and Howe.<sup>6</sup> 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<sup>7</sup> 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  $\text{cm.}^{-1}$ , and a weaker transition at 61,850  $\text{cm.}^{-1}$  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  $\text{cm.}^{-1}$ , for which we have obtained an integrated absorp-

tion 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  $\text{CF}_4$  was probably  $\text{CF}_3\text{Cl}$ . To determine whether the absorption could be partly due to  $\text{CF}_3\text{Cl}$ , spectrograms were taken with the sample cooled with freezing baths at temperatures of  $-80$ ,  $-130$  and  $-189^\circ$ . Since  $\text{CF}_3\text{Cl}$  has a lower vapor pressure than  $\text{CF}_4$ , the partial pressure of  $\text{CF}_3\text{Cl}$  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.<sup>8</sup> 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.

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