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Effect of Pressure on Intensity of Some Electronic Transitions in SF_6, C_2H_2 and C_2D_2 Vapors in the Vacuum Ultraviolet Region[1]

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The absolute intensities of four separate electronic transitions of SF_6 in the region 1850 to 780 Å. have been measured quantitatively by methods of photographic photometry. Three of these transitions were fitted to a Rydberg series with an ionization limit of 16.15 e.v. Experimental f-numbers for these transitions were found, and f for the lowest energy transition was compared with a value calculated with approximate wave functions. The effect of rotational structure of electronic transitions on the integrated absorption coefficients was studied for part of this transition. This effect was studied also for a transition near 65800 cm.$^{-1}$ in C_2H_2 and in C_2D_2. The same experimental f-number was found for both molecules, and the value was independent of the pressure.

The electronic absorption spectrum of SF_6 was obtained first by Liu, Moe and Duncan,[3] who found four resolved transitions with maxima all below 1100 Å. Rough qualitative estimates of f-numbers were given, and some speculations were advanced about the nature of the electronic transitions. Results of the present work allow a more definite formulation of the former ideas, by providing quantitative measurements of the integrated absorption coefficients of the transitions.

The rotational structure which accompanies an electronic transition may lead to extreme variations of transmitted intensity in a range of frequencies covered by a spectrograph slit of finite width. As a consequence the usual spectrograph, which certainly cannot resolve this structure completely, measures an absorption coefficient which may be far from the true value. This effect is well known for the case of rotation–vibration spectra in the infrared, and methods for correction have been discussed.[4] Inert gases are added to reduce the intensity at the rotational lines, and the true integrated absorption coefficient is obtained by extrapolation to zero pressure (at constant path length). The effect becomes apparent when the integrated absorption coefficients increase with increase of partial pressure of absorbing gas. In electronic transitions, total absorption is reached frequently at very low pressures, which limits the range of study of this factor. Addition of inert gases also causes experimental difficulties at very short wave lengths, where windows cannot be used between light source and absorbing column. Attempt has been made nevertheless in the present work to use as far as possible the pressure broadening and extrapolation techniques which have been used in the infrared. Some transitions in SF_6, C_2H_2 and C_2D_2 have been examined in this way, and results are reported here.

Experimental Details

Materials.—The stated purity of the SF_6 gas obtained from the Matheson Company was 99%. Further purification was accomplished as in former work.[3] The principal impurity remaining was SO_2, but this impurity was reduced to a maximum of 0.04% as shown by mass spectrometer examination. C_2D_2 was prepared by the action of 99.75% D_2O on "Special High Purity" grade calcium carbide.[5] The carbide was extracted with CCl_4 for eight hours and then was baked in vacuum for 48 hours to remove H_2O and other absorbed gases. D_2O vapor was circulated over the purified carbide, and the C_2D_2 was condensed and dried by passage through three traps at −80°. The C_2D_2 finally was fractionally sublimed in vacuum, and only the middle fraction was used. Stitt,[6] who used a similar method with 99.5% D_2O, found that the acetylene evolved contained 98.5% C_2D_2 and 1.47% C_2HD, by mass spectrometer analysis. C_2H_2 was prepared in the same way from distilled H_2O.

Procedure.—The method used by Moe and Duncan[7] was followed and the same vacuum spectrograph, with one meter grating at about normal incidence, was used also. Absorption coefficients were obtained at a very large number of accurately known wave lengths. A direct current hydrogen discharge tube operated at constant intensity was used as a background down to 980 A. Measurements at lines in the H_2 band spectrum below 1650 Å. assured accuracy in frequency. The frequency at which absorption coefficients above 1650 A. were measured is subject to some error, since the background is continuous above 1650 Å., but the coefficients are extremely small in this region and do not make an appreciable contribution to integrated coefficients. Below 980 Å., the CuI spectrum from a hollow cathode discharge was used.[8] The slit width was 0.06 mm. in all experiments, which corresponds to a band of frequencies about 22 cm.$^{-1}$ wide at 1500 Å. and 89 cm.$^{-1}$ wide at 750 Å. The path length of absorption was about 200 cm. in all experiments.

When inert gases were added to study the effect of pressure on integrated absorption coefficients, the gas mixture had to be separated from the light source by a CaF_2 window, which did not transmit below 1240 Å. The effect of pressure could be studied only above this wave length.

Results and Discussion

Absorption coefficients of SF_6 were obtained at more than 200 wave lengths between 780 and 2200 Å., in a pressure range of 0.002 to 158 mm. The experimental results, based on 14 plates, are shown in Table I. The f-numbers were calculated from the formula

$$f = (mc^2/n\pi e^2)\int \alpha_\nu d\nu = 4.20 \times 10^{-8} \int \alpha_\nu d\nu \quad (1)$$

α_ν is the absorption coefficient in cm.$^{-1}$ at N.T.P. at a frequency ν in cm.$^{-1}$. The four transitions are broad continuous regions which overlap slightly. The number of points at which the coefficients were measured is more than sufficient to show the de-

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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] Ta-kong Liu, G. Moe and A. B. F. Duncan, *J. Chem. Phys.*, **19**, 71 (1953).

[4] E. B. Wilson, Jr., and A. J. Wells, *ibid.*, **14**, 578 (1946).

[5] Obtained from the National Carbon Co. and stated by them to be not less than 90% pure.

[6] F. Stitt, *J. Chem. Phys.*, **8**, 56 (1940).

[7] G. Moe and A. B. F. Duncan, THIS JOURNAL, **74**, 3136 (1952).

[8] A. G. Shenstone, *Phil. Trans. Roy. Soc.* (*London*), **A235**, 195 (1936).

tailed shapes of the absorption curves with considerable accuracy. The coefficients between the transitions decreased sufficiently so that fairly accurate correction could be made for the overlapping, except for the overlap of the last transition with the continuous absorption following. This continuum, below which nothing can be resolved, is estimated here to begin at 812 Å., which is in no essential disagreement with the value 802 Å. reported previously.

TABLE I

ELECTRONIC TRANSITIONS IN SF_6

Transition	I	II	III	IV
Approx. ν_{max} (cm.$^{-1}$)	94600	107050	115200	122300
Corresponding wave length (Å.)	1057	934	870	817
Band width (cm.$^{-1}$)	20400	8500	12300	4900
No. of independent measurements of f	7	5	5	4
Experimental f	0.294	0.055	0.130	0.097
Computed f	0.86 1.19	...	...	...
Computed ν_{max} (eq. 2)	94483	...	115805	122512

Former measurements[3] indicated slight absorption up to about 2170 Å., and the possibility of an additional weak transition between 1600 and 2200 Å. was carefully investigated. The present results show that the absorption coefficients of the lowest energy transition decrease in a regular way from $\alpha_\nu = 616$ at the maximum (1057 Å.) to 50 at 1200 Å. α_ν then decreases slowly to a value about 1 cm.$^{-1}$ at 1420 but is unreliably small above this wave length, and is effectively zero near 1850 Å. The wave numbers of absorption maxima in Table I agree well with the former results[3] for the first two transitions. Somewhat different results are obtained of the other two transitions, especially for the fourth, which is found here to lie about 1850 cm.$^{-1}$ higher than in the former result.

With improved values for the maxima of the third and fourth transitions, it is found that transitions I, III and IV fit the Rydberg formula

$$\nu = \nu_\infty - R/(n + 0.75)^2 \quad (n = 1, 2, 3) \qquad (2)$$

The fit is shown in Table I. Higher members could not have been seen in the continuous absorption beginning at about 123000 cm.$^{-1}$. ν_∞ in formula 2 is 130316 cm.$^{-1}$ (16.15 e.v.), which is in harmony with the estimate (16.0 e.v.) from former work[3] and a theoretical value (20.1 e.v.) obtained by Duncan.[9]

An approximate computation was made of the f-number of the lowest energy transition, based on the molecular orbital functions calculated in that work.[9] It was found there that the highest energy orbital occupied in the normal state was doubly degenerate, with a symmetry type E_g. The two orbital functions, ϕ_2 and ϕ_3 of the same energy are two linear combinations of $(2p\sigma)_F$ and $(3d)_S$ atomic orbitals, and each is occupied by two electrons with opposite spin in the normal state of the molecule. The experimental f-value indicates that the electronic transition is allowed, and the upper electronic state is therefore $^1F_{1u}$. The orbital to which the electron is excited is called ϕ_e, and must be orthogonal to the other molecular orbitals and belong to the symmetry type $^1F_{1u}$. Since the electrons which remain in closed shells during the optical transition will not contribute to the transition moment,[10] the problem is reduced to a calculation of the moment between two states represented by four-electron configurations, and the excitation may be formulated as

$$(\phi_2 \text{ or } \phi_3)^4,\ {}^1A_{1g} \longrightarrow (\phi_2 \text{ or } \phi_3)^3(\phi_e),\ {}^1F_{1u} \qquad (3)$$

Furthermore it was shown here that use of ϕ_2 or ϕ_3 gave identical final results, and subsequent notation may be simplified by specific use of ϕ_3. After reduction of the four-electron integral over the state functions, the moment is Qe, with $Q^2 = Q_x^2 + Q_y^2$ and

$$\begin{aligned} Q &= 2\int \phi_3 r \phi_e \, dV \\ &= 2\sqrt{2}\int \phi_3 x \phi_e \, dV \qquad (4) \\ \phi_3 &= 0.893(3d_{x^2-y^2})_S + 0.179(\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5) \\ \phi_e^{I} &= 0.777(3p_x)_S - 0.718(\sigma_2 - \sigma_3) \\ \phi_e^{II} &= (4p_x)_S \end{aligned}$$

The atomic orbitals in 4 are

$$\begin{aligned} (3d_{x^2-y^2})_S &= (c_3^7/6\pi)^{1/2} r^2 e^{-c_3 r} \sin\theta \cos 2\phi \\ (4p_x)_S &= (c_4^9/105\pi)^{1/2} r^3 e^{-c_4 r} \sin\theta \cos\phi \\ \sigma_i \begin{pmatrix} x \\ y \end{pmatrix} &= (c_F^5/\pi)^{1/2} r\, e^{-c_F r} \sin\theta \begin{pmatrix} \cos\phi \\ \sin\phi \end{pmatrix} \\ c_3 &= Z^*(3d)_S/3a_0 = 1.0393 \\ c_4 &= Z^*(4p)_S/4a_0 = 0.4724 \text{ (ref. 11)} \\ c_F &= Z^*(2p)_F/2a_0 = 4.9131 \end{aligned}$$

σ_2, σ_3, σ_4, σ_5, are $(2p)_F$ directed along the axes x, y, $-x$, $-y$, respectively, toward the S atom.

The final results are: with ϕ_e^I, $f = 0.86$; with ϕ_e^{II}, $f = 1.19$. These values are about three and four times the experimental value $f = 0.29_1$ but closer agreement is not expected with the approximate functions used.

It was found that the absorption coefficients integrated over part of the first transition (from 1250 to 1300 Å.) were independent of the partial pressure of SF_6, as is shown in Table II. The variation of pressure of SF_6 was as large as could possibly be

TABLE II

EFFECT OF PRESSURE ON INTEGRATED ABSORPTION COEFFICIENT (I) OF SF_6 BETWEEN 1250 AND 1300 Å.

p_{SF_6}	p_{He}	I, cm.$^{-2}$
0.033	0	5.82×10^{-4}
.067	0	6.83×10^{-4}
.125	0	6.59×10^{-4}
.055	100	6.58×10^{-4}
.073	100	6.24×10^{-4}
.137	100	6.52×10^{-4}
.053	133	6.52×10^{-4}
.098	133	6.19×10^{-4}
.141	133	6.73×10^{-4}
.073	370	6.33×10^{-4}

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(9) A. B. F. Duncan, *J. Chem. Phys.*, **20**, 951 (1952).

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

(11) $n = 4$ rather than $n = 3.7$ was used for greater convenience in evaluation of two-center integrals resulting from expansion of equation 4 with ϕ_e^{II}, but the difference should not be great.

carried out in the 200 cm. absorption column in this particular region. Also it is realized that only a small part of the first transition has been examined for the effect of pressure. However, since the rotational structure fails to cause any apparent pressure dependence in the part observed, there is no reason why the remainder of the transition should show a pressure dependence.

The effect of pressure was investigated also in analogous transitions of C_2H_2 and C_2D_2 which occur with maxima at 65790 and 65880 cm.$^{-1}$. The electronic transition in the two molecules is surely the same, and involves excitation of an electron from the C≡C bond, possibly to a Rydberg $3d\delta$ orbital.[6] Hence it is expected that integrated absorption coefficient and f-number should be the same in the two molecules. However, the rotational spacing should be smaller in C_2D_2, and there should be about 38% more rotational lines in a slit width than with C_2H_2. If rotational structure has an effect on integrated absorption coefficients in this transition, it should become apparent in a difference in the f-numbers for the two molecules at the same pressure. It was found, however, that the f-numbers were exactly the same within experimental error. Furthermore, f-numbers for the two molecules were individually pressure independent, and the values were not modified by moderate additions of helium. C_2D_2 was studied only at two pressures because of the limited supply. The electronic transition contains in each case three broad resolved vibrational transitions, and the coefficients at the peaks of the latter are considerably higher than coefficients in SF_6. For this reason the upper pressure limit of acetylene was set at a low value, so that points near the top of the peaks could be measured. Data are given in Table III.

TABLE III

INTEGRATED ABSORPTION COEFFICIENT EXPRESSED AS f-VALUE FOR THE 65800 CM.$^{-1}$ TRANSITION IN C_2D_2 AND IN C_2H_2

C_2D_2 (ν_{max} = 65880 cm.$^{-1}$)			C_2H_2 (ν_{max} = 65790 cm.$^{-1}$)		
$p_{C_2D_2}$	p_{He}	f	$p_{C_2H_2}$	p_{He}	f
0.0026	0	0.128	0.0022	0	0.130
0.0050	0	0.132	.0037	0	.128
			.0022	26	.128
			.0022	44	.127
			.0022	80	.130

It may be argued that the range of pressures in every case considered here was too limited to show any variation of f with pressure. But it must be pointed out that the range of equivalent path lengths here is as wide, and has the same order of magnitude as in the infrared measurements, where very definite pressure dependence is found. It must be concluded in the cases examined here that sufficient reduction of the intensity peaks of rotational lines must have occurred at very low pressures, and that the f-numbers for these cases are not seriously in error because of this factor. This conclusion certainly should not be generalized, even to include other electronic transitions in the molecules considered here.

Finally, a correction should be made to the previous work on measurement of f-numbers in acetylene,[7] where the value f = 0.062 was reported for the transition discussed above, and the value f = 0.13 is found here. In the former work, the acetylene was introduced from a large calibrated volume into the spectrograph through a small bore stopcock, and it is believed that insufficient time was allowed for diffusion, and perhaps not all the measured volume of acetylene entered the spectrograph. In the present work this error was avoided. The corrected value agrees more closely with the theoretical value given in the former work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange and Aquation Studies with Thiocyanato Complexes[1]

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The first-order aquation rate constants for the replacement of thiocyanate by water have been determined for the complex ions $Cr(NH_3)_5(SCN)^{++}$, $Co(NH_3)_5(SCN)^{++}$ and *trans*-Co $en_2(SCN)_2^{+}$. For the first two, the respective values in min.$^{-1}$ are $k = 1.17 \times 10^{13} \exp(-24{,}900/RT)$ and $k = 0.85 \times 10^{13} \exp(-26{,}800/RT)$, with $\Delta S^{\ddagger} = -7.8, -8.4$ e.u. The rate of bimolecular exchange of thiocyanate ion with the $SC^{14}N$ labeled complexes was found to be not more than a few per cent. of the aquation rates, being undetectable against the aquation background. The aquation of $Co(NH_3)_5(SCN)^{++}$ was found to be catalyzed by thiocyanate ion while for $Cr(NH_3)_5(SCN)^{++}$ no such enhancement of rate was found. An interpretation of this and other aspects of ligand replacement with trivalent chromium and cobalt complexes is presented whereby it is inferred that an S_N2 mechanism holds for chromium complexes and an S_N1 mechanism for those of cobalt.

During recent years renewed interest has developed in the nature of the mechanisms whereby one ligand replaces another in covalently bonded complex ions. Evidence has been sought in exchange studies and in the kinetics of net reactions. Thus the rapid exchange of ligand with $Ni(CN)_4^{-2}$,[2,3] $Pd(CN)_4^{-2}$ [2] and PtX_4^{-2} [2,4] ions has been thought to result from a ready bimolecular reaction involving a five coördinated transition state employing the available outer p-orbital.[5,6]

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(1) These investigations were carried out under contract N6onr 23809 between the University of Southern California and the Office of Naval Research. They were presented at the Symposium on Coördination Chemistry, Copenhagen, August, 1953.

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(3) F. A. Long, *ibid.*, **73**, 537 (1951).

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