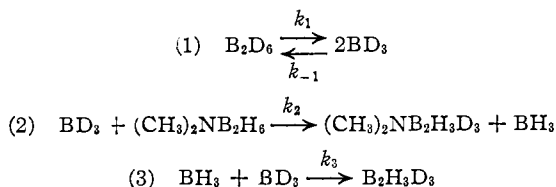The fractional order with respect to diborane indicates that the diborane is dissociating into two fragments one of which in turn reacts with the dimethylaminodiborane. A mechanism consistent with these results is

$$(1) \quad B_2D_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2BD_3$$

$$(2) \quad BD_3 + (CH_3)_2NB_2H_6 \overset{k_2}{\longrightarrow} (CH_3)_2NB_2H_3D_3 + BH_3$$

$$(3) \quad BH_3 + BD_3 \overset{k_3}{\longrightarrow} B_2H_3D_3$$

It is interesting to note that once again the kinetic results of this study have forced one to assume the existence of a BH_3 intermediate. The nature of the intermediate in the rate-determining step is also of interest. The structure of dimethylaminodiborane is represented by
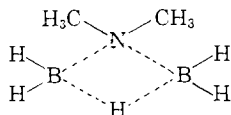
When one considers this, an intermediate which would be consistent with the results of this work would be a structure represented by
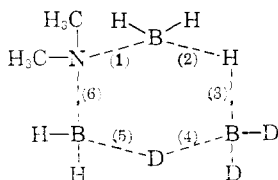
A triangular intermediate such as this has been mentioned previously. A plausible structure

for such a species has been given[7] to be three BH_2 groups held together with three bridge hydrogens.

If we let the above structure represent the intermediate, then the products formed are dependent upon which bonds rupture. The rupture of bonds numbered (1) and (3) would lead to dimethylaminodiborane which is deuterated in two terminal positions and in the bridge position. The rupture of bonds numbered (4) and (6) would lead to dimethylaminodiborane which is deuterated in two terminal positions only. The rupture of bonds numbered (2) and (4) would lead to deuteration of the bridge position only, while the rupture of bonds numbered (3) and (5) would represent no isotopic change.

The observed activation energy was 27.8 kcal. The observed value of course includes the heat of reaction of elementary step 1 above. Then

$$E_{obsd.} = 27.8 \text{ kcal.} = E_2 + \frac{1}{2}(E_1 - E_1)$$

The quantity $(E_1 - E_{-1})$ has been estimated[8] to be equal to 28.4 ± 2 kcal. Assuming this is correct, the activation energy for the rate-determining step, E_2, would equal 13.6 kcal.

Compared to results obtained from studies of similar systems such as the self-deuteration of diborane, this activation energy is quite high and probably arises in part from the difference in strengths of the B–H–B bond in DMADB and diborane.

The consistency of this exchange mechanism and the nature of the intermediate is amenable to further experimental confirmation by studying the kinetics of boron isotopic exchange in this reaction. It is expected that such measurements will be made in the near future.

(7) W. H. Eberhardt, B. Crawford and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954).

(8) S. H. Bauer, THIS JOURNAL, 78, 5775 (1956).

The Fluorescence of Sulfur Dioxide[1]

BY KENNETH F. GREENOUGH[2] AND A. B. F. DUNCAN

Fluorescence spectra of SO_2 are obtained for the first time by direct optical excitation to the second electronic state above the normal state. Transitions are observed to vibrational levels of the normal state from vibrational levels of both the second and the first excited electronic states. The latter state could not be populated directly because of low absorption coefficients. The fluorescence spectrum of microcrystalline SO_2 at 77°K. was found to be identical with the vapor spectrum. The mean lifetime associated with transitions from the second to the normal state was found to be a linear function of the pressure in the range 0.017 to 0.0005 mm. The lifetime extrapolated to zero pressure is 4.2×10^{-5} second. The lifetime of the first excited state could not be determined from the vapor because of low intensity, but a value of about 5×10^{-4} second was obtained from the solid at 77°K. Only the order of magnitude of this value may have qualitative significance.

Introduction

Absorption spectra of SO_2 have shown the existence of several electronic transitions in the spectral

region 1800 to 3900 Å. The transition to the first excited electronic state above the normal state has an origin at 3880 Å. and a maximum intensity at 3740 Å.[3] The intensity of the transition as a whole is very weak. The origin of the transition to the second excited state above the normal state is at 3376 Å., with a maximum intensity at 2940 Å.[4] The intensity of this transition is quite strong. These two transitions have been

(3) N. Metropolis and H. Beutler, Phys. Rev., 57, 1078 (1940).

(4) N. Metropolis, ibid., 60, 295 (1941).

well resolved from each other. A third absorption region extends from 2400 to 1800 Å. The nature of the electronic states of SO_2 have been discussed by Walsh[5] and by Mulliken[6] on the basis of semi-quantitative molecular orbital theory.

The fluorescence spectrum of SO_2 is not as well understood. Lotmar[7] observed fluorescence which resulted from excitation by monochromatic light of about 2100 Å., at SO_2 pressures of 0.5 to 20 mm. Excitation in this case was to electronic states higher than the second, and the fluorescence spectrum extended from about 2100 Å. to the blue. Lotmar proposed an interpretation of the details of the structure of the spectrum below 2500 Å. He was unable to observe fluorescence resulting from light absorption in any other spectral region, and he concluded that fluorescence did not occur from what are called the first and second excited states in this work. Norrish and Zeelenburg[8] produced SO_2 in excited states by flash photolysis of H_2S,O_2 mixtures, and they observed a continuous emission from the blue to about 2000 Å., which they associated with fluorescence of excited SO_2 molecules. It should be noted also that emission spectra of SO_2 have been obtained in electric discharges by a number of workers[9-14] Smyth[15] has correlated these spectra with the results of Lotmar.

No observations of fluorescence resulting from direct optical excitation to the first or to the second excited states have been reported. In view of the complexity of Lotmar's spectrum, it appeared possible that some of the transitions did originate on these levels, contrary to his interpretation. Accordingly the fluorescence spectrum of SO_2 was re-examined, and further attempts were made to populate the first and second electronic levels directly.

Experimental Details

1. **General.**—An anhydrous grade of SO_2 was distilled, outgassed several times in a vacuum system and stored. A sample of a definite pressure and volume was allowed to expand into the fluorescence cell through a series of calibrated volumes. Pressures were measured directly with mercury manometers. All measurements were made at prevailing room temperature (no control), except as noted below.

The fluorescence cell for gases was made from a cylindrical brass tube, 7.5 cm. diameter and 15 cm. long, with plane fused quartz windows of somewhat larger diameter sealed on end flanges with Apiezon W wax. A short brass side tube, 7.5 cm. diameter, was attached perpendicular to the main tube and was centered at the midpoint of the main tube. The side tube was also closed with a fused quartz disc about 8 cm. diameter. The cell was internally blackened to reduce scattered radiation. The cell was attached to the glass vacuum line with a metal-glass seal. The pressure rise from desorbed gases was negligible.

(5) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(6) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

(7) W. Lotmar, *Z. Physik*, **83**, 765 (1933).

(8) R. G. W. Norrish and A. P. Zeelenburg, *Proc. Roy. Soc. (London)*, **A240**, 293 (1957).

(9) T. C. Chow, *Phys. Rev.*, **44**, 638 (1933).

(10) A. G. Gaydon, *Proc. Roy. Soc. (London)*, **A146**, 901 (1934).

(11) G. Kornfeld, *Trans. Faraday Soc.*, **32**, 1487 (1936).

(12) R. C. Johnson and W. H. B. Cameron, *Proc. Roy. Soc. (London)*, **A106**, 195 (1924).

(13) V. Henri and J. Wolff, *J. de Physique et Radium*, **10**, 81 (1921).

(14) E. V. Martin, *Phys. Rev.*, **41**, 167 (1937).

(15) H. P. Smyth, *ibid.*, **44**, 690 (1933).

A General Electric A-H 6 mercury arc served as the source of excitation. Light passed first through a Farrand ultraviolet monochromator, adjusted to pass a band from 2700–3100 Å., then along the long axis of the cell. This band matched closely the major part of the absorption spectrum corresponding to transition from the normal to the second excited electronic state of SO_2. The available path length was not sufficient for excitation to the first electronic state by monochromatic light of wave lengths greater than 3800 Å.

The efficiency of this monochromator was high and consequently SO_2 vapor was exposed to very intense radiation for fairly long periods. The question of possible photochemical decomposition naturally arises and was considered carefully. We have ample evidence that no large amount of decomposition occurred. The visible fluorescence and presumably the ultraviolet fluorescence also disappeared and reappeared on alternate condensations and reevaporation of SO_2 with the same intensity, after repeated exposures. There was no detectable change in pressure. These measurements are of limited sensitivity but could have detected about 1% decomposition. The best modern thermochemical data show that no primary decomposition of SO_2 into $SO + O$ is possible at the wave lengths used. A reaction of excited SO_2 with normal SO_2 or with Hg vapor is thermochemically possible. Such reactions provide an explanation of some early observations[16] on decomposition with λ3130. There are no modern data on photochemical decomposition below 1 mm. pressure, which might answer the questions directly.

Of more importance is the effect of slight decomposition of SO_2 on the present results. To have any significant effect on the fluorescence spectrum, one or more of the products would have to be produced in excited states. Since there is barely enough energy for decomposition into products in their normal states, subsequent excitation either directly or by energy transfer from excited SO_2 appears improbable. Quenching and lifetime of fluorescence could be effected by normal products but only if they removed energy preferentially from excited SO_2. This possibility cannot be excluded but we can see no reason why it is probable.

2. **Fluorescence Spectrum.**—The spectra were photographed at right angle to the exciting beam with a Hilger E484 spectrograph. Exposures were over 20 hr. at a slit width of 0.05 mm. The best spectra of the vapor were obtained in a pressure range of 0.01 to 1.0 mm. The SO_2 sample was replaced every 2 hr. There appeared to be no photochemical decomposition of SO_2. Spectra also were obtained from the microcrystalline solid frozen at 77°K. in a quartz tube about 6 mm. diameter. In this case special precautions in diaphragming, focussing and angle of view were taken to reduce scattering and reflection of the incident light. Exposure times were a few minutes at the above slit width.

3. **Quenching of the Fluorescence.**—Observations of intensity of fluorescence of SO_2 in the 3200–3800 and 3800–5000 Å. regions were made with RCA 1P28 and 1P21 photomultiplier tubes, respectively. The respective wave length regions were isolated by a Corning 5860 and a Wratten 47 B filter. No attempt was made to take photometric measurements below 3200 Å. because of the large amount of scattered incident radiation. Above 3200 Å., the intensities were corrected for scattered radiation from readings with the cell empty. The addition of the inert foreign gases had no measurable effect on the amount of scattered light. The two photocells were placed side by side in front of the middle window of the fluorescence cell and they were masked to receive only light which originated from within the cell. The anode currents of the photocells were measured with a microammeter. The current was directly proportional to the intensity of the fluorescent radiation, for both cells.

SO_2 was admitted to the fluorescence cell at a measured pressure, and the intensity of fluorescence was measured with both cells. The SO_2 was then frozen out in a side arm and the inert gas admitted at a measured pressure. The cold trap then was removed and the gases allowed to mix at room temperature. An opaque shield was then removed

(16) K. Wieland, *Trans. Faraday Soc.*, **30**, 260 (1934); references to earlier observations are found here.

from the source and the fluorescence intensity measured. This procedure was repeated at constant pressure of SO_2 for a series of pressures of the inert gases. The inert gases were "analytical grade" CO_2, H_2, O_2 and He, which were taken directly from cylinders.

4. Lifetime of the Fluorescence.—A sample of SO_2 vapor was illuminated by an intense flash of light, produced by discharge of a capacitor through a xenon filled tube 1.2 mm. diameter and 6 mm. long.[17] The capacitor was charged to 3000 volts, and there was sufficient resistance in the circuit to prevent spontaneous discharge. The flash tube was triggered manually by an external pulse from a Tesla-type spark coil. The flashes were reproducible, with a rise time of less than one microsecond and decayed effectively to zero in less than 5 microseconds. A band of 2700–3100 Å. radiation from the flash was obtained through the monochromator, and the decay of fluorescence from the second excited state was observed with a photomultiplier-oscillograph combination.[18] A filter in front of the photomultiplier limited the radiation received to the 3200–3800 Å. region. The decay curve was photographed and its co-ordinates could be measured with considerable precision and an accuracy limited primarily by the calibration of the timing marks. The average deviation from the mean in the lifetime measurements was about 3%, over a range of 0.0005 –0.017 mm. pressure of SO_2.

Fluorescence from the first excited state could not be measured by this method. Instead, a collimated beam, properly filtered, from a 450 watt, direct current mercury arc was focussed on a sample of solid SO_2 at 77°K. The source was interrupted periodically by a rotating sector at 7.8 millisecond intervals to give pulses of 2.6 millisecond duration. The individual pulses had rise and decay times of less than 0.3 millisecond. A 1P21 photomultiplier tube with filters was used to isolate the 3800–5000 Å. fluorescence region. The oscillograph sweep was synchronized with the rotating sector and the stationary trace of fluorescence decay was displayed and photographed.

Results

1. Fluorescence Spectrum.—Nine strong transitions appear in the 2800–3100 Å. region along with some scattered Hg radiation. The latter prevents accurate measurement of transitions near the 2950.9 and 2975.2 Å. Hg lines. The transitions are recorded in Table I, column 1. The over-all

TABLE I

FLUORESCENCE SPECTRUM OF SO_2 (WAVE LENGTHS IN Å.)

Transitions from second excited state		Transitions from first excited state
Resonance	Weak group	
2883.9	3181	3837 (weak)
2912.2	3205	3886.9
2929.8	3229	3966.1
2954.7	3282	4007 (weak)
2966.5	3307	4047.6
2991.9	3331	4064.7
3011.7	3354	4155.3
3051.2		4216 (weak)
3075.7		4241.6
		4265.8
		4334 (weak)
		4368.7
		4452

effect of increasing the pressure of SO_2 from 0.13 to 1.00 mm. is a general reduction in the intensities of these transitions. There is an unresolved region of continuous emission from below 3000 to above 4400 Å. Seven very weak transitions (Table I, column 2) are superimposed on the part of the continuous region from 3181–3354 Å. These transi-

(17) H. Edgerton and P. Cathou, *Rev. Sci. Instr.*, **27**, 821 (1956).

(18) D. Neuberger and A. B. F. Duncan, *J. Chem. Phys.*, **22**, 1693 (1954).

tions appear to be a continuation of the group in column 1 but are poorly defined because of low intensity. A system of discrete bands between 3887 and 4452 Å., shown in Table I, column 3, appears superimposed on the long wave length end of the continuous region. The thirteen transitions are observed at SO_2 pressure between 0.13 and 1.0 mm. At higher pressure the individual bands broaden.

2. Quenching of Fluorescence.—The fluorescence intensities in both wave length regions increase with SO_2 pressure up to about 0.01 mm. and then decrease at higher pressures. Figure 1 shows curves which are typical of this qualitative behavior. Quenching from the first excited state could not be studied independently because of overlapping of transitions from the second excited state, and no quantitative data are reported. Some quantitative data on quenching from the second electronic state were obtained, in the pressure range 0.0005 up to about 0.001 mm., which showed that the intensity depended linearly on the pressure. The low pressure data could be extrapolated accurately up to about 0.05 mm. pressure of SO_2 and provided information on self-quenching of SO_2. The self-quenching data thus obtained follow a Stern–Volmer relation

$$(I^0/I) - 1 = bp = z\tau \qquad (1)$$

where I^0 and I are the intensities of fluorescence in the absence and in the presence of quenching molecules respectively; z is the number of quenching collisions per excited molecule per sec. per cc. and is proportional to p, the pressure of quenching molecules; τ is the mean lifetime of the excited state and b is a constant. The value of b is determined from a plot of (I^0/I) against pressure and was found to have the value 212 mm.$^{-1}$ at room temperature. It is convenient to consider the pressure p^* at which $I = 0.5\ I^0$. Then $p^* = 1/b = 0.0047$ mm., and $\tau = 1/z$.

Equation 1 probably is not valid above about 0.05 mm. pressure of SO_2. We estimate that the fraction of light absorbed at this pressure is less than 2%, but at 0.5 mm. the fraction is 15% and at 6.0 mm. the fraction is 73%. These values are estimated from the geometry of the system, from which it is probable that all fluorescence is measured which originates in a path between 1 and 12 cm. from the front window which receives the incident light. The absorption coefficient at the maximum, $\alpha = 20$ cm.$^{-1}$ (path length in cm. at 0° and 76 cm. pressure) was used in the estimate. These fractions are too large for quantitative treatment of the high (>0.05 mm.) pressure data of Fig. 1, but the upper curve shows qualitatively that self-quenching is large for the 3200–3800 Å. region.

By a somewhat involved argument, which will not be given here, it is possible to show that self-quenching also occurs after excited molecules have been transferred from the second to the first excited electronic state. By reasonable assumptions about the magnitude of quenching constants involved, it appears that self-quenching should be less important in the 3800–5000 Å. region, in
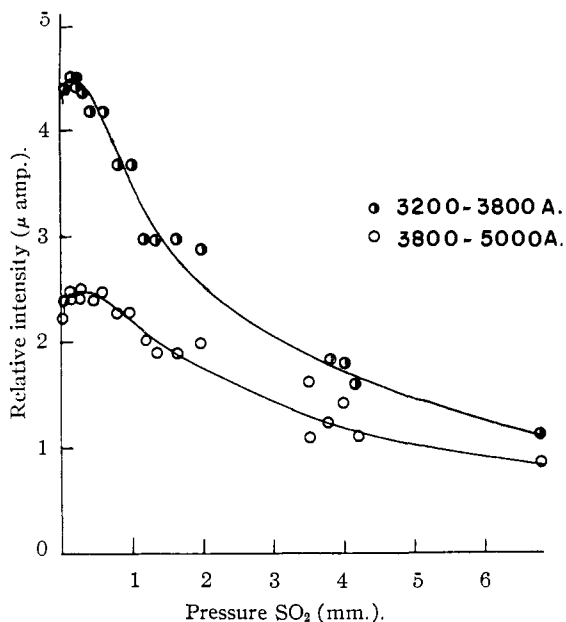
Fig. 1.—Fluorescence intensity as a function of SO_2 pressure.

qualitative agreement with the experimental results in Fig. 1.

Strong quenching of the SO_2 fluorescence is produced by the addition of CO_2, while H_2, O_2 and He are less effective, in the order given. Representative data for CO_2 at various fixed pressures of SO_2 are shown in detail in Table II. These data may

TABLE II

RELATIVE FLUORESCENCE INTENSITIES AT FIXED PRESSURES OF SO_2 AS A FUNCTION OF CO_2 PRESSURE, DERIVED FROM CURVES OF ORIGINAL DATA

Pressure of CO_2 (mm.)	Pressure of SO_2 (mm.)					
	0.055		0.13		0.29	
	3200–3800 Å.	3800–5000 Å.	3200–3800 Å.	3800–5000 Å.	3200–3800 Å.	3800–5000 Å.
0.00	100	100	100	100	100	100
.10	40	26	74	56	69	59
.20	27	15	44	40	58	47
.30	21	12	33	30	49	39
.40	16	9	27	23	42	36
.50	12	..	23	19	38	33
.60	10	..	19	15	34	27
.70	8	..	17	12	32	23
.80	7	..	15	9	29	21
	0.64		0.92		4.20	
0.00	100	100	100	100	100	100
.10	88	64	96	77	..	..
.20	79	54	92	71	..	..
.30	71	49	86	65	..	..
.40	65	46	82	60	..	..
.50	59	43	77	55	..	..
.60	54	41	73	51	..	..
.80	46	37	67	43	94	93
10.00	..	..	..	..	~50	

be treated in a way similar to the self-quenching data and may be represented by a series of equations, all of the form

$$(I^0/I) - 1 = k_m(M)/(k_s(SO_2) + k_f)$$

$$= bp = z\tau \qquad (2)$$

where I_0 and I are now the intensities of fluorescence in the absence and in the presence of a quenching inert gas at pressure p; k_m, k_s, and k_f are rate constants for removal of excited SO_2 by collision with inert gas by self-quenching and by fluorescence, respectively. Application of equation 2 to quenching by CO_2 gives a family of straight lines; each line corresponds to a fixed pressure of SO_2 and each line has zero intercept. A value of p^* is calculated for each pressure of SO_2 and these values of p^* are extrapolated to zero pressure of SO_2 to give a value of CO_2 quenching in the absence of SO_2 self-quenching. Effective quenching cross sections (σ^2) for the collisional deactivation processes can be evaluated from the usual gas kinetic expressions and equation 2, provided τ is known. By use of the experimental value reported below, we find for quenching of SO_2 fluorescence by CO_2, p^* at zero pressure SO_2 is 0.030 mm. and σ^2 is 1.59×10^{-16} cm.^{2} These effective cross sections can be compared with gas kinetic cross sections calculated from molecular collision diameters determined from gas viscosity measurements.[19] For SO_2 self-quenching, the gas kinetic cross section is defined here as the square of the molecular collision diameter and equals 18.8×10^{-16} cm.^{2}; for CO_2 quenching of SO_2 fluorescence, the gas kinetic cross section is defined here as the square of one-half the sum of the molecular collision diameters of the two molecules and equals 17.4×10^{-16} cm.^{2} ($SO_2 = 4.34$, $CO_2 = 3.99 \times 10^{-8}$ cm.).

Essentially every collision between normal and excited SO_2 molecules in the second excited electronic state is efficient in quenching; only one in ten collisions between CO_2 and excited SO_2 is effective, since σ^2 is proportional to z. The self-quenching of SO_2 fluorescence is nearly 20 times as efficient as quenching by CO_2 molecules.

3. Lifetime of Fluorescence.—It was found that the experimental lifetime (τ) depended on the pressure, and $1/\tau$ was a linear function of the pressure below 0.017 mm. Actual measurements were made down to 0.0005 mm. pressure of SO_2. A value of τ_0, the purely radiative lifetime, was obtained by extrapolation of the $1/\tau$ values to zero pressure. For the second excited electronic state, a value of $\tau_0 = 4.2 \pm 0.2 \times 10^{-5}$ second was found. The mean lifetime of the first excited state could not be measured in SO_2 vapor because of the very low intensity of fluorescence. Since the intensity is greatly enhanced in the solid, a lifetime was determined from a sample of SO_2 at 77°K. The average of a number of values found in this way is $5.0 \pm 1.0 \times 10^{-4}$ second. Qualitative experiments at higher temperatures but below the melting point show that τ decreases with increasing temperature and presumably becomes longer at lower temperatures.

Discussion

1. Fluorescence Spectra.—The nine strong resonance transitions have been observed also in absorption spectra of SO_2 at low pressures. Metro-

(19) J. Hirschfelder, C. Curtiss and R. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954. p. 599.

polis[4] and Clements[20] have identified these transitions as $\nu''_{1,2,3} = 0$ to $\nu'_{1,2,3} > 0$. The wave lengths of the associated weaker transitions correspond with absorption bands observed also by Metropolis. The intensity ratios of the weak transitions as a whole in the fluorescence spectrum are approximately the same as intensity ratios of corresponding absorption transitions reported by Metropolis and Clements. Since the dimensions of the molecule undergo a marked change in the second excited electronic state,[5,6] it is possible that a large number of transitions have similar energies and consequently overlap. This overlapping probably accounts for the continuous fluorescence observed.

Eleven of the transitions between 3887 and 4452 Å. are related to transitions from the zero level of the first excited state to excited levels of the ground state. A tentative assignment of these transitions is presented in Table III, based on com-

TABLE III

ANALYSIS OF FLUORESCENCE TRANSITIONS FROM FIRST EXCITED STATE

Transition (cm.$^{-1}$)	Assignment				Frequency difference	
	$\nu'_{2,1}$	ν''_1	ν''_2	ν''_3	obsd.	calcd.
25727(3886.9 Å.)	0	0	0	0	0	0
25214	0	0	1	0	513	518
24706	0	0	2	0	1021	1036
24602	0	1	0	0	1125	1151
...	0	0	3	0	..	1554
24066	0	1	1	0	1661	1669
23719	0	0	4	0	2008	2072
23576	0	1	2	0	2151	2187
23464	0	2	0	0	2285	2302
23073	0	0	5	0	2654	2590
22890	0	2	1	0	2837	2820
22462	0	3	0	0	3265	3453

binations and harmonics of the symmetrical bending frequency, $\gamma_2 = 518$ cm.$^{-1}$ and the symmetrical stretching frequency, $\gamma_1 = 1151$ cm.$^{-1}$.[21,22] Since the infrared spectrum indicates that there is very little anharmonicity evident in the ground state vibrational levels, all of the above assignments show agreement within experimental error. Only the transition at 4452 Å. shows appreciable deviation from the calculated frequencies; however, this transition is weak and is poorly defined. The $3\nu_2$ transition may be present but obscured by overlap of the strong transition at 4155.3 Å. Two transitions which do not fit into the above scheme are observed at 3837 and at 4007 Å. These transitions originate probably in the first excited vibrational level of the excited state; the frequency separation between them is 1102 cm.$^{-1}$ and probably correspond to the ν_1 (1151 cm.$^{-1}$) stretching frequency.

The over-all intensity of this fluorescence system increases from the origin at 3886.9 to a maximum at 4155.3 Å., which is the $(\nu_1 + \nu_2)$ combination, and decreases at longer wave lengths. This distribution of intensity provides confirmation that there is only a small change in dimensions of the

first excited state relative to the ground state. This conclusion was drawn from the corresponding absorption spectrum by Metropolis[23] and Coffman.[24]

The ground state data derived from the present work are in good agreement with other data obtained from the fluorescence spectrum observed by Lotmar[7] and the electric discharge emission spectrum observed by Chow.[9] The three levels tentatively associated with the unsymmetrical frequency $(\nu_3 b_1) = 1370$ cm.$^{-1}$) by Lotmar and Chow do not appear in the present work. In the older work, these transitions are associated with the second and higher excited electronic states, while the transitions observed in the present work are associated with the first excited state only.

The long wave length fluorescence system is identical in almost every detail with the emission spectrum observed as an afterflow by Gaydon[10] with an electric discharge in SO_2 at pressures less than 5 mm. A comparison of both of these with the long wave length portion of the fluorescence spectrum of Lotmar shows scattered coincidences, but these may be fortuitous because of the very large number of transitions in this region observed by Lotmar.

The fluorescence spectrum of the solid at 77°K. is identical with the vapor spectrum except for two features. The individual vibrational transitions are less well resolved. But transitions from the second excited state in the 3500–3800 Å. region are effectively absent. At the same time, transitions from vibrational levels of the first excited state are less evident than transitions from the zero level, and this results in a simplification of the spectrum.

2. Quenching of Fluorescence.—The relative quenching efficiency by inert gases is in the order CO_2, H_2, O_2 and He for the fluorescence of SO_2 in its first excited state. The fact that O_2 shows no apparent preferential quenching is of interest in connection with observation of lifetime of this state (see below). Lotmar also observed quenching of fluorescence excited by wave lengths 2100 Å. with these and other gases. It is difficult to draw any comparison of his data on quenching with the present data, because it is not known how much of Lotmar's data were associated with molecules which may have been transferred to lower excited electronic levels before quenching occurred.

3. Lifetime of Fluorescence.—The values of the lifetime of fluorescence from the second excited electronic state may be compared with values calculated from integrated absorption coefficients. τ_0 was calculated as 2.0×10^{-7} from absorption data obtained in this Laboratory. Other values, 2.1 and 3.0×10^{-7}, are obtained from data quoted by Mulliken.[4] Such a comparison is somewhat artificial since it assumes that the initial and final vibrational levels concerned in absorption and emission are the same, which is not the case here. A comparison with absorption data for the first electronic transition can be made only with our

(20) J. H. Clements, *Phys. Rev.*, **47**, 224 (1935).

(21) M. K. Wilson and R. S. Polo, *J. Chem. Phys.*, **22**, 900 (1954).

(22) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 285.

(23) N. Metropolis, *Phys. Rev.*, **60**, 283 (1941).

(24) M. F. Coffman, J. M. Corgan, C. M. Loyd and J. B. Coon, *Bull. Am. Phys. Soc.*, [2] **1**, 91 (1956).

measurement on the solid at 77°K. If the effect of temperature decrease could be associated definitely and uniquely with reduction of non-radiative processes, such as amplitudes of crystal vibrations, then it might be possible to obtain a significant value of τ_0 by extrapolation of measured τ at various low temperatures. A more thorough study of this point will be made, but the necessary equipment is not available at present. Values of τ_0 from absorption data, quoted by Mulliken, range from 1.3×10^{-2} to 2.2×10^{-3}, and are considerably longer than our value 5×10^{-3} second.

But the orders of magnitude of τ_0 associated with the two electronic states of SO_2 show at least that the first excited state has a longer lifetime than would correspond to the usual singlet–singlet transition. This suggests that the first excited state may be a triplet state. Douglas[25] has observed an effect of a magnetic field on the first electronic state but no such effect on transition to the second electronic state. He attributed his observations to a triplet character of the first excited state. We observed no preferential quenching of the fluorescence from the first excited state by O_2, but the pressure of O_2 probably was not sufficiently high, and our observation is not sufficient for rejection of the hypothesis that the first excited state may be a triplet.

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The Activation Energies of Proton Transfer Reactions in Ammonium and Methylammonium Solutions Measured by the Nuclear Magnetic Resonance Technique[1]

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The activation energies of proton transfer processes of the types (R = H or Me)

$$R_3NH^+ + NR_3 \longrightarrow R_3N + HNR_3^+$$

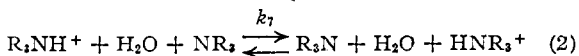$$R_3NH^+ + H_2O + NR_3 \longrightarrow R_3N + H_2O + HNR_3^+$$
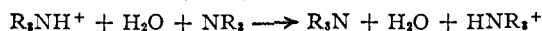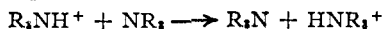
have been measured by the nuclear resonance technique in aqueous solutions of ammonium and methylammonium chlorides and have values very close to zero. An activation energy of 12.2 ± 0.5 kcal. mole^{-1} was found for the reaction

$$NH_4^+ + H_2O \longrightarrow H_3O^+ + NH_3$$
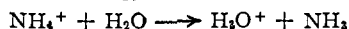
The significance of these results in terms of diffusion controlled reaction mechanisms is discussed. The thermodynamic functions ΔH^*, ΔF^* and ΔS^* have been calculated for these reactions and indicate that for those reactions where $\Delta E \simeq 0$. the free energy of activation is $\simeq 5$ kcal. mole^{-1}.

The rates and mechanisms of proton transfer reactions have been studied previously in aqueous solutions of ammonium[4-6] and methylammonium[7,8] ions at room temperature by the nuclear magnetic resonance (n.m.r.) technique. We have extended these studies by measuring the proton transfer rates as a function of the temperature and have evaluated the activation energies associated with these processes.

It was found[4-8] that the main contribution to the total rate of exchange can be attributed to the mechanisms

$$R_3NH^+ + NR_3 \underset{}{\overset{k_6}{\rightleftarrows}} R_3N + HNR_3^+ \qquad (1)$$

$$R_3NH^+ + H_2O + NR_3 \overset{k_7}{\rightleftarrows} R_3N + H_2O + HNR_3^+ \qquad (2)$$

where R denotes the methyl or hydrogen radicals in the ammonium or methylammonium ions. The

notation of the rate constants is the same as that used in references 5–8. The ratio k_6/k_7 was found[6,8] to be independent of the ammonium or methylammonium concentrations.

Two additional exchange mechanisms are the direct proton exchange between the ammonium ion and the hydroxyl ions or the water molecules, respectively. The first of these is a very fast reaction[9] ($k_5 \simeq 10^{11}$ sec.$^{-1}M^{-1}$), but its contribution to the total rate of exchange is negligible because of the small concentration of the hydroxyl ions in the pH range in which the rates were measured (pH 1 to 4). The second reaction (exchange with water) is a very slow reaction in both the ammonium and methylammonium cases. However, the rate in ammonium solutions[6] ($k_4 = 24.4$ sec.$^{-1}$) is large compared with the rate in methylammonium solutions[8] ($k_4 = 1.2$ sec.$^{-1}$), and hence its contribution to the total rate has been considered only in the former case and the activation energy associated with this process has been evaluated.

The n.m.r. spectra of ammonium and methylammonium solutions at room temperature and the changes they undergo as a function of pH have been described elsewhere.[4-8] The changes in the line shapes of the spectra as the temperature of the solution is raised are similar to those which are observed when the hydrogen ion concentration of

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