CHEMILUMINESCENCE AND PHOTOLUMINESCENCE OF S_2, SO AND SO_2 IN SF_6 AFTERGLOWS

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Summary

Frequently, the success of producing short-lived chemical species for use in chemical kinetic studies or for obtaining spectroscopic data depends on the chance finding of a source which gives high density of molecules. This paper describes methods of obtaining chemiluminescence of S_2, SO and SO_2 molecules, and, as well, sufficiently large concentrations of these species in their ground states to make possible the spectroscopic study by white light photoluminescence. A mixture of sulfur hexafluoride in helium passing through a microwave discharge serves as a source of these reactive atoms and molecules.

Experimental

The experimental set up is shown in Fig. 1. Two stainless-steel tube crosses (10 cm i.d.) with O-ring connectors provided a convenient observation chamber. Two fused silica windows (W) and a series of baffles (D) in a right angle arrangement allowed optical access. All inner surfaces were painted black. Emission from the center region of the chamber was focused on the entrance slit of a grating monochromator by the quartz lens (L). Dispersed radiation was detected by a photomultiplier (PM) in conjunction with an amplifier and chart recorder. A 150 W xenon lamp (X) directly in front of window (W_2) was used to produce photoluminescence. Chemiluminescence was generated by a microwave discharge through SF_6 in helium. The discharge took place in a Pyrex tube (A). Fluorine atoms from SF_6 in the discharge

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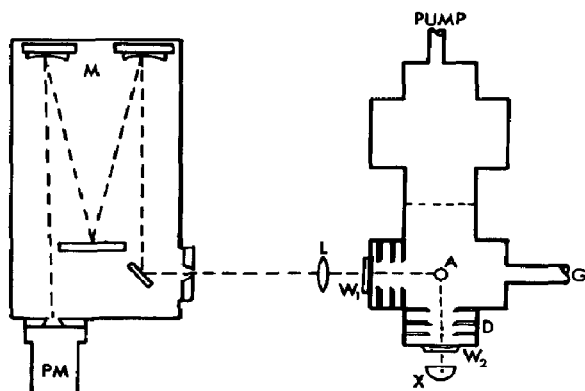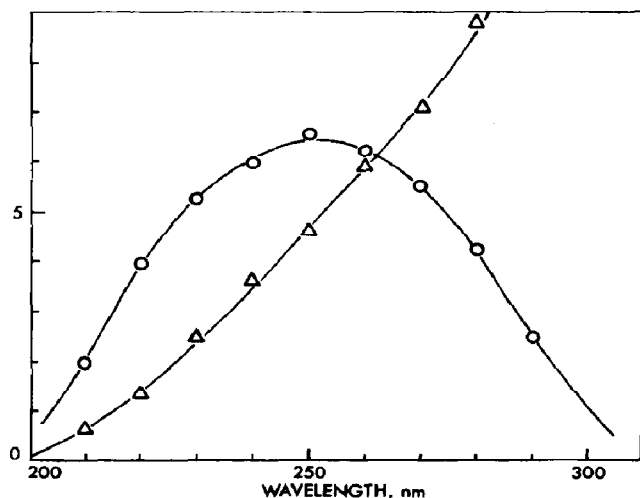
Fig. 1. Experimental arrangement.

Fig. 2. Instrumental response. O, Relative spectral response per photon of the detection system. The decrease in spectral response at longer wavelengths is caused by a combination of grating blaze and a solar blind photomultiplier tube. △, Relative photon flux of the xenon lamp.

slowly removed material from the Pyrex walls; a small hole was formed in 10 - 12 h of discharge operation. Connection to the chamber was made by a Teflon (1/4 in. i.d.) tubing. Concentrically around the Teflon was a Pyrex tube through which reactant gases (H_2O, H_2O_2, O, O_2, O_3) could be admitted. Also, gases could be added through another inlet (G). The pump was a 7 l/s mechanical pump. Pressure was measured by a diaphragm type instrument.

Relative spectral response of the monochromator/photomultiplier combination was determined by measuring the intensities of NO_γ ($A^2\Sigma^+ \to X^2\Pi$) band photoluminescence as excited by the xenon lamp [1]. The xenon lamp's relative flux vs. wavelength was determined by measuring its intensity and correcting for the relative response of the optical system (Fig. 2).
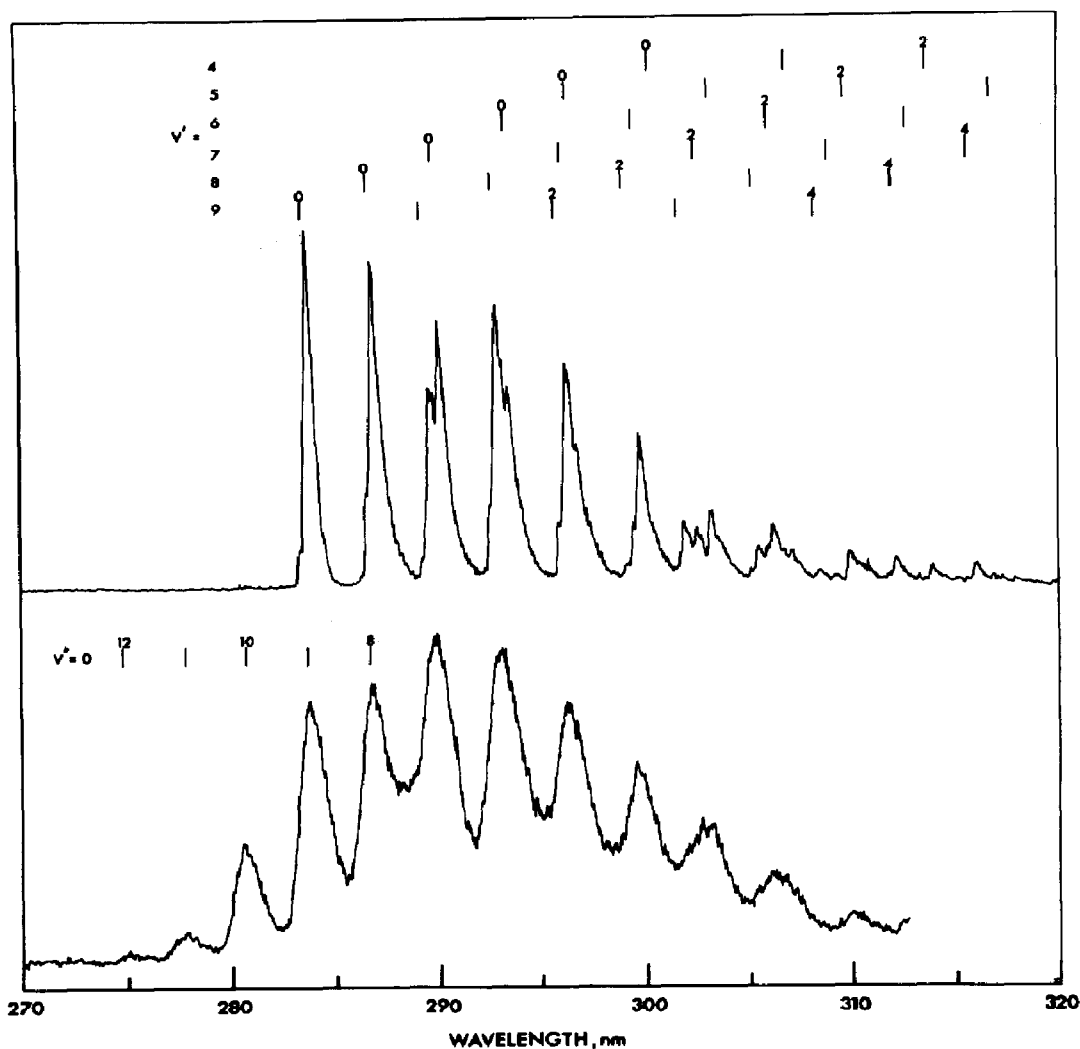
Fig. 3. (a) S_2 photoluminescence with a resolution of 0.4 nm at a helium pressure of 1.5 Torr and (b) S_2 chemiluminescence with a resolution of 1.6 nm at a helium pressure of 7 Torr.

Results

Photoluminescence and chemiluminescence spectra of S_2, SO and SO_2 were recorded under a variety of conditions. Results are conveniently divided according to the molecule studied.

$S_2 (B^3 \Sigma_u^- \rightarrow X^3 \Sigma_g^-)$

S_2 (B → X) emission was easily observed in the SF_6 afterglow in photoluminescence (Figs. 3a and 4) and chemiluminescence (Fig. 3b). Different series of v'' progressions are observed [2]. Chemiluminescence spectra are similar to the photoluminescence spectra but the 10-0, 11-0, and 12-0
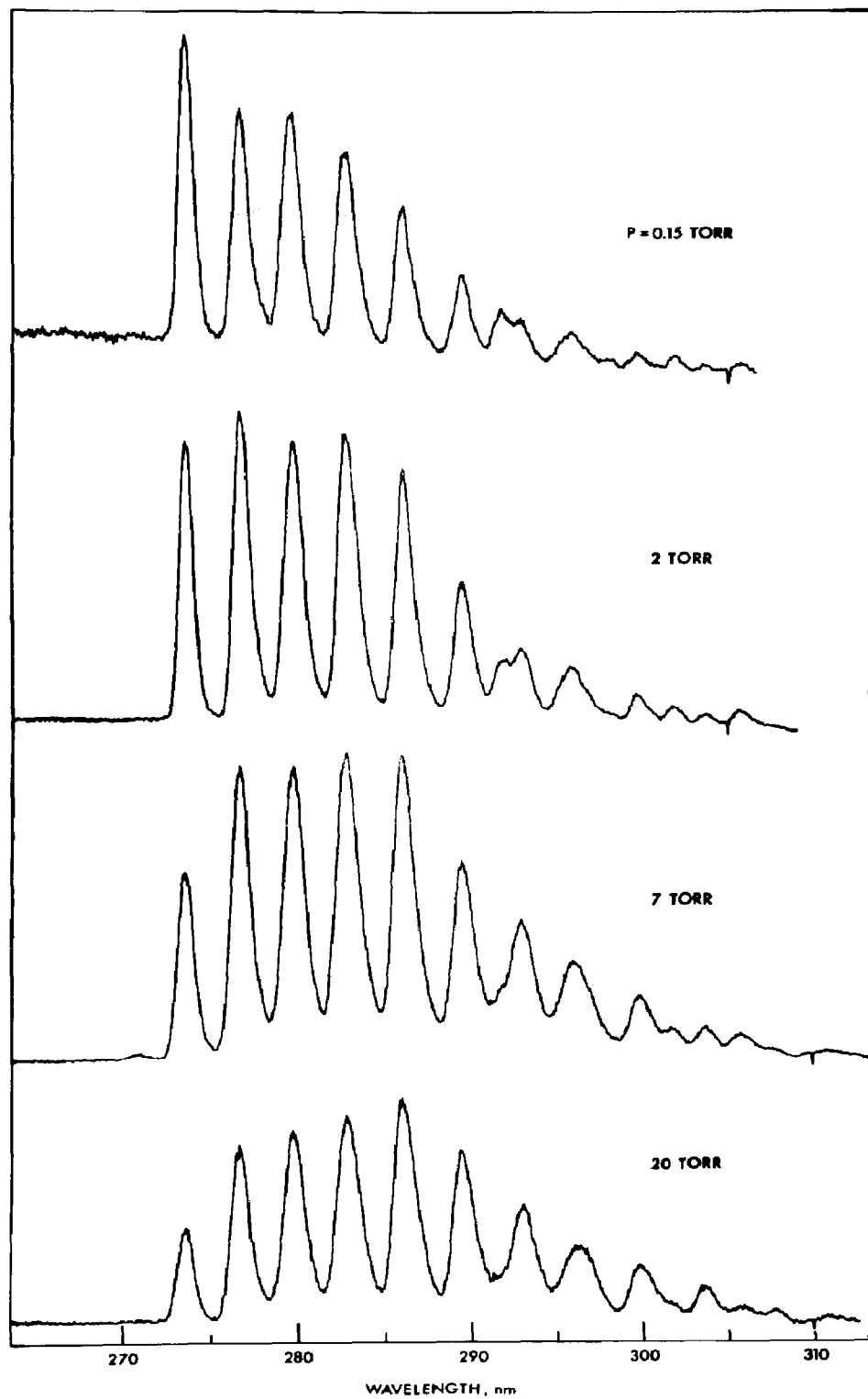
Fig. 4. Effect of pressure on S_2 photoluminescence with a resolution of 0.8 nm.

TABLE 1

Measured intensities and relative band strengths of S_2
from white light photoluminescence

v', v''	I	$I_{v',v''}$[a]	$q_{v',v''}$[b]	I_ν	$S_{v',v''}$
9.0	78	22	3.74	71	2.7
9.1	42	18	6.69		
9.2	8	6	1.64		
9.3	11	11			
9.4	3	6			
8.0	70	23	2.80	65	2.7
8.1	61	31	6.82		
8.2	10	7	3.69		
8.3	8	11			
7.0	58	24	1.94	58	2.7
7.1	35	21	6.23		
7.2	11	11	5.80		
7.3	2	4			
6.0	40	20	1.22	54	2.4
6.1	33	22	5.06		
6.2	11	16	7.16		
5.0	30	21	0.69	44	2.5
5.1	15	15	3.60		
5.2	7	34	7.18		

[a]Peak intensity (Fig. 3) divided by relative spectral
sensitivity (Fig. 2).
[b]Calculated Franck–Condon factors from Ref. 3.

transitions are additional features which are relatively enhanced at lower pressure. Since the present experiments emphasize spectral emission below 300 nm, long wavelength spectra are not included. However, with a different grating–photomultiplier combination, S_2 spectra have been observed to beyond 500 nm.

Measured intensities of the first members of different progressions as taken from Fig. 3a are given in Table 1. No emission from $v' > 9$ could be detected in the photoluminescence. Vibrational relaxation in the B state is observed at He pressures above 1 Torr (Fig. 4).

Relative band strength factors $S_{v',v''}$ can be obtained from measured emission intensities $I_{v',v''}$ and the intensity of the exciting light at the frequency of the transition I_ν. The intensity $I_{v',v''}$ of a band and the population $N_{v'}$ of the v' level are related by the equation:

$$I_{v',v''} \propto N_{v'} q_{v',v''} \nu^3 R_e^2 (\bar{r})$$

(1)

where $q_{v',v''}$ is the Franck–Condon factor, ν is the frequency of the emitting transition, and $R_e(\bar{r})$ is the electronic transition moment. In first approximation

$$N_{v'} \propto q_{v',v''} \nu R_e^2 (\bar{r}) I_\nu / (A_{v'} + [M] k_{v'})$$

(2)

where $A_{v'}$ is the Einstein A value of level v', $k_{v'}$ is the quenching coefficient for vibrational level v' and [M] is the density of the quenching molecules. Since the production of excited $S_2(B^3\Sigma_u^-, v')$ is governed mainly by pumping from $S_2(X^3\Sigma_g^-, v'' = 0)$, the populating of excited states is primarily from $v'' = 0$. For v', $v'' = 0$ transitions, ν is the same for emission and absorption and eqns. (1) and (2) can be solved for $S_{v',0}$:

$$S_{v',0} \equiv R_e^2(\bar{r})q_{v',0} \propto \left(\frac{I_{v',0}}{\nu^4 I_\nu}\right)^{1/2} (A_{v'} + [M]k_{v'})^{1/2} \qquad (3)$$

Within experimental error limits, measured radiative lifetimes of the B state of S_2 for $v' = 0$ - 4 are independent of v' [4, 5]. If the lifetimes for higher v' also do not depend on v', and if $k_{v'}$ is independent of v', then $A_{v'} + [M]k_{v'}$ is independent of v' and need not be considered for relative values of $S_{v',0}$. Relative values of $S_{v',0}$ are given in Table 1. It is important to note that only the ratio of $I_{v',0}/I_\nu$ need be known, eliminating the need for knowledge of the instrumental spectral response.

Meyer and Crosley [4] in comparing measured [4, 6] and calculated [7, 8] Franck–Condon factors, found that the experimental factors are 4 times larger than the calculated RKR values. The present measurements indicate a similar discrepancy. For example, if RKR Franck–Condon factors are used to derive the relative population $N_{v'}$, from the measured intensities (Table 1), the populations obtained from the first member of each progression is about two times larger than those obtained from the next member. Also, measured band strength factors $S_{v'v''}$ within the v', 0 sequence for $5 \leqslant v' \leqslant 9$ give Franck–Condon factors (assuming $R_e(\bar{r})$ = constant) that are constant and do not agree with the RKR values.

Relative vibrational populations $N_{v'}$ obtained from the chemiluminescent intensity measurements are shown in Fig. 5. $N_{v'}$ was obtained by assuming that $S_{v',0} \simeq$ constant for $v' \geqslant 9$ since it was experimentally found that band strength factors within a v' sequence were constant for $5 > v' > 9$ (Table 1). The production of excited $S_2(B^3\Sigma_u^-)$ by chemical reaction yields a vibrational population which for $v' > 9$ gives the same straight line in a logarithmic plot for pressures of 2 and 7 Torr. From the slope, a vibrational temperature of 375 K is obtained. The spectral resolution was not sufficient for measuring relative vibrational distributions for $v' \leqslant 7$.

Fair and Thrush [9] have proposed that $S_2(B^3\Sigma_u^- v = 10)$ is formed via inverse predissociation from ground state sulfur atoms in a two body process:

$$S(^3P) + S(^3P) \to S_2(B^3\Sigma_u^- v = 10)$$
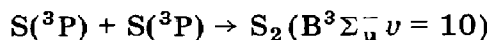
The present results heavily favor this inverse predissociation mechanism. Although we have not made attempts to explore the kinetics of the SF_6 afterglow, the observed $S_2(B \to X)$ emission is very likely produced by $S_2(B^3\Sigma_u^-)$ formed by S atom recombination. Chemical reactions which could produce excited S_2, such as:
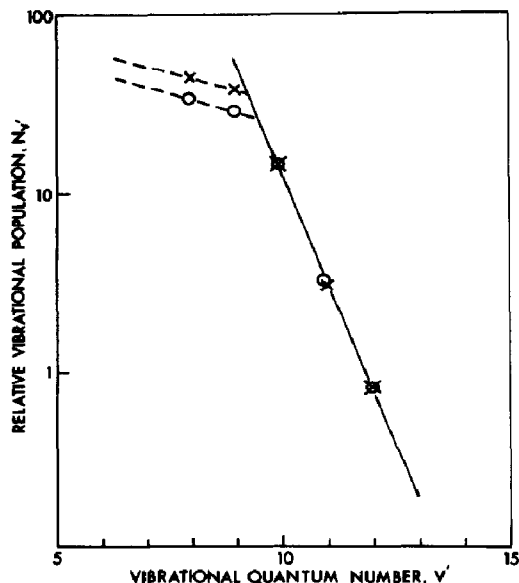
$$S + SF \to S_2^* + F$$
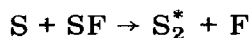
Fig. 5. Relative vibrational populations, $N_{v''}$, of $S_2(B^3\Sigma_u^-)$. ×, From data obtained at 7 Torr; ○, from data obtained at 2 Torr. $q_{v,0}$ has been assumed to be constant.

cannot give enough energy to the S_2 molecule to account for excitation of the B state to $v' \geqslant 10$.

Figure 5 also contains information that can be used to obtain the dissociation energy of S_2. While populations of levels $v' = 10$, 11 and 12 are pressure independent, levels $v' < 10$ are pressure dependent and thus are not produced by the inverse predissociation mechanism. The relative population of molecules formed by inverse predissociation for $v' > 9$ is given by:

$$N_v \propto K_{eq}^{v'} \frac{k^{v'}}{k^{v'} + k_s + (M)k_q^{v'}} \tag{4}$$

where $K_{eq}^{v'}$ is the equilibrium constant for the formation of level v' from atoms, k^v is rate coefficient for recombination, k_s is the radiative deactivation rate coefficient, and $(M)k_q^{v'}$ stands for collisional deactivation of level v'. An estimate of k^v can be obtained from the fact that no photoluminescence from $v' > 9$ has been observed; thus $k^{v'} \gg k_s$.

Furthermore, the uncertainty principle together with Herzberg and Mundie's observation [10] of the diffuseness of $S_2(B - X)$ absorption bands at $v \geqslant 10$ can be used to obtain an upper limit for $k^{v'}$. While the 11,0 band was quite diffuse, diffuseness in the 10,0 band could not be observed but was inferred on the basis of an increased absorption strength. Diffuseness usually means that the width of an individual line becomes comparable to the spacing between adjacent rotational lines. The rotational spacing in $S_2(B - X)$ is about 2 cm^{-1} and thus, $\Delta E \simeq 1$ cm^{-1} for lines in the 11,0 transition. On the other hand, diffuseness could not be observed in the 10,0 band; a rough estimate for ΔE could be 0.1 cm^{-1}. Accordingly, $k^{10} < 2 \times 10^{10}$ s^{-1} and $6 \times 10^7 \ll k^{10} \leqslant 2 \times 10^{10}$. Even at the highest total pressures, the $(M)k_q^{v'}$ term in

eqn. (4) cannot compete with $k^{v'}$. Therefore, relative vibrational population of levels $v' > 9$ are given by the dependence of the equilibrium constant on vibrational energy. This is confirmed by our experiment.

From the slope of the straight line in Fig. 5, $hc\omega/kT = 1.439$ is derived. Since the vibrational constant ω in the vicinity of $v' = 11$ is 376 cm^{-1}, the vibrational temperature is 375 K. The slight increase of T over the room temperature is probably caused by the heating of the gas in the discharge. Figure 5 shows that much of the population at $v' = 9$ is not formed by inverse predissociation. Its relative population is pressure dependent and cannot be fitted to the $N_{v'} \propto K_{eq}^{v'}$ behavior. The fact that N_9 lies lower than the value given by a slight extrapolation of the straight line connecting $v' = 10 - 12$ must mean that the contribution due to inverse predissociation observed at $v' = 9$ is small. Taking the measured value as an upper limit of formation by inverse predissociation, it can be inferred that the S_2 dissociation energy is at least equal to the sum of the energy of $v' = 9$ plus 188 cm^{-1}. The latter number is the rotational energy $v' = 9$ needs to bring its total energy (electronic + vibration + rotation) to the dissociation limit. The S_2 dissociation energy is thus found to be: $(35372 + 188) < D_0^\circ < 35754$ or $D^\circ(S_2) = 35657 \pm 100$ cm^{-1} = 100.95 ± 0.3 kcal/mol. This value is very close to the value of 101.7 ± 0.4 kcal/mol discussed by Fair and Thrush [9].

$SO(B^3\Sigma^- \to X^3\Sigma^-)$

When products of a discharge through SF_6 in helium were mixed with trace amounts of H_2O_2, SO(B → X) photoluminescence (Fig. 6a) and chemiluminescence (Fig. 6b) were observed. Band heads of positively identified transitions are marked [2]. Transitions from $v' > 3$ have not previously been observed in emission.

In the chemiluminescence spectrum, intensities of the $(0, v'')$ progression of SO and of the lower members $(v'' < 4)$ of the $1, v''$ progression are very weak. The most intense bands in the spectrum belong to the $2, v''$ and $3, v''$ progressions. Moreover, in spectral regions not obscured by large intensities from the $2, v''$ and $3, v''$ progressions, some members of the $4 - 8, v''$ progressions are observed. Identification is aided by comparing the intensities in individual v'' progressions with published Franck–Condon factors [11]. There also is underlying continuous chemiluminescence emission due to SO_2 (see later).

Photoluminescence was much more intense than chemiluminescence and could be observed with no confusing underlying chemiluminescence. The spectrum consists of the $0 - 3, v''$ progressions. Only two members (0,4 and 0,5) of the $0, v''$ progression are observed. Resolution greater than that of Fig. 6a showed that the contribution of 0.4 at the wavelength of the 2.5 band was less than 10% of the latter; and the measured intensity of the 2.6 band was not greatly affected by the overlapping of the 0,5 band. Furthermore, many bands from $v' > 3$ were positively identified. However, intensities were always less than 5% of the strong transitions from $v' \leqslant 3$. At wavelengths greater than 280 nm the spectrum is obscured by the much stronger S_2 (B → X)
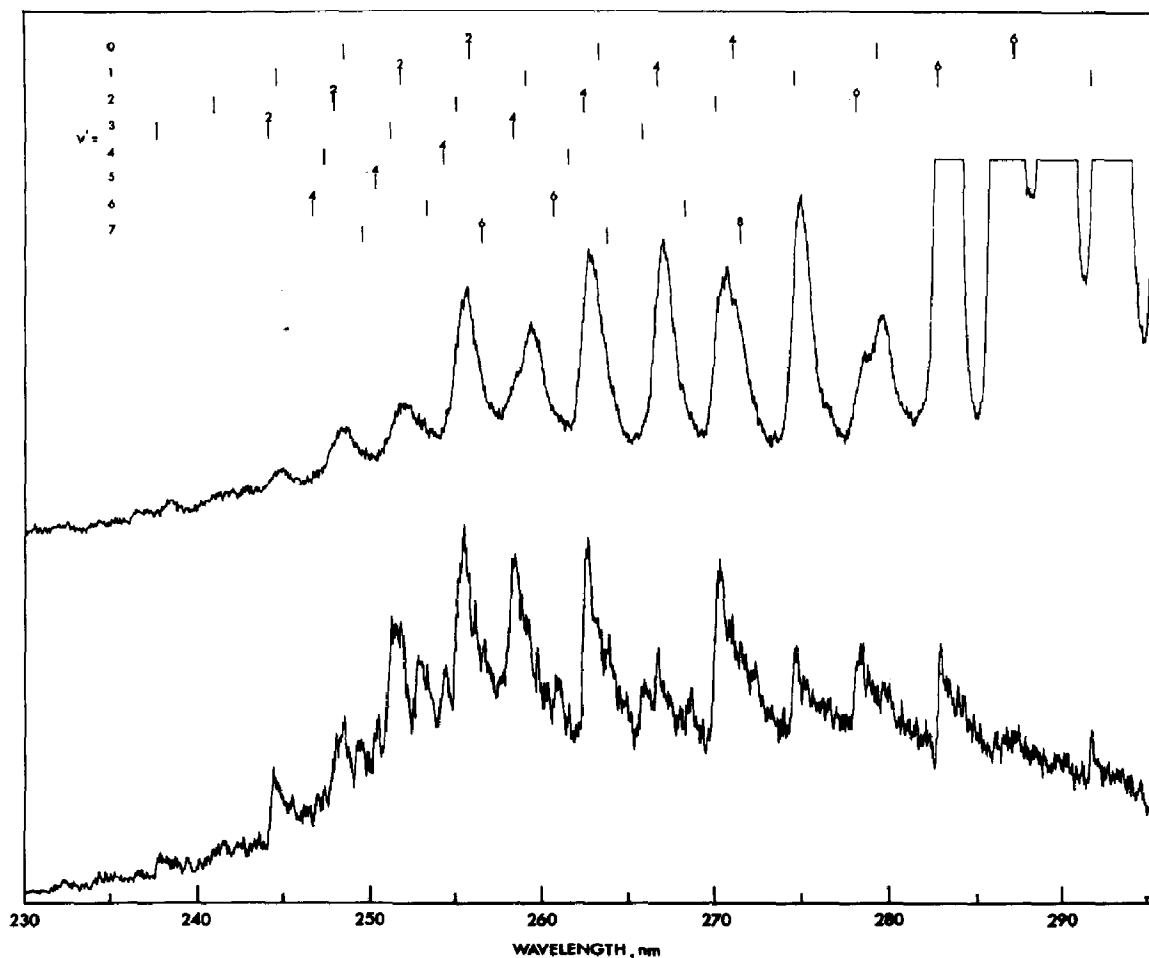
Fig. 6. (a) SO photoluminescence with a resolution of 1.6 nm at a helium pressure of 3.3 Torr and (b) SO chemiluminescence with a resolution of 0.4 nm at a helium pressure of 3.0 Torr.

photoluminescence. Peak band intensities of SO divided by the instrument's spectral response are given in Table 2.

TABLE 2

Measured photoluminescence band intensities of SO

v''/v'	0	1	2	3
0				
1				
2		15	18	10
3		40	54	20
4		87	73	21
5	65	115	80	
6			47	

Hebert and Hodder [11] have measured relative integrated emission intensities of 26 bands of the SO(B → X) transition. The measurements were interpreted with computed Franck–Condon factors and r-centroids to determine first the variation of the electronic transition moment $R_e(\bar{r})$ with effective nuclear separation and secondly to obtain a smoothed array of band strength factors. Their $R_e(\bar{r})$ curve was mainly derived from measurements of $v' = 0$ and $v' = 1$ progressions for the range of 218 nm $< R_e(\bar{r}) <$ 417 nm.

Our results do not confirm the measurements of Hebert and Hodder since our measurements follow the variation of RKR Franck–Condon factors whereas large discrepancies are found for Hebert and Hodder's band strength factors. The conclusion then is that the electronic transition moment is constant for at least 8 bands [(2,3), (2,4), (2,5), (2,6) and (1,2) (1,3), (1,4), (1,5)]. Figure 7 compares $R_e(\bar{r})$ values as functions of the r-centroid. $R_e(\bar{r})$
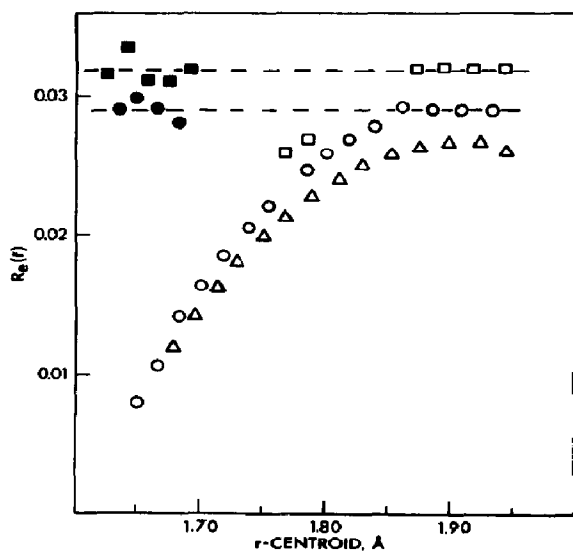

Fig. 7. Relative electron transition moments $R_e(\bar{r})$ for SO. △, ○, □, From ref. 11 for $v' =$ 0.1 and 2, respectively. ●, ■, From the present work for $v' = 1$ and 2 respectively.

values from the present measurements are scaled to those of Hebert and Hodder at $\bar{r} > 1.85$ Å. The reason for the large discrepancies is not obvious. We only speculate that the spectral response function in Hebert and Hodder's work was not properly determined.

SO_2 chemiluminescence

When diluted or pure SO_2 passed through a microwave discharge, the chemiluminescence produced by the three body recombination:

$$SO + O + M \rightarrow SO_2 + h\nu$$
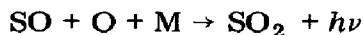
is observed downstream. In the present study, SF_6 diluted by helium was passed through the discharge and a number of different oxygen containing gases
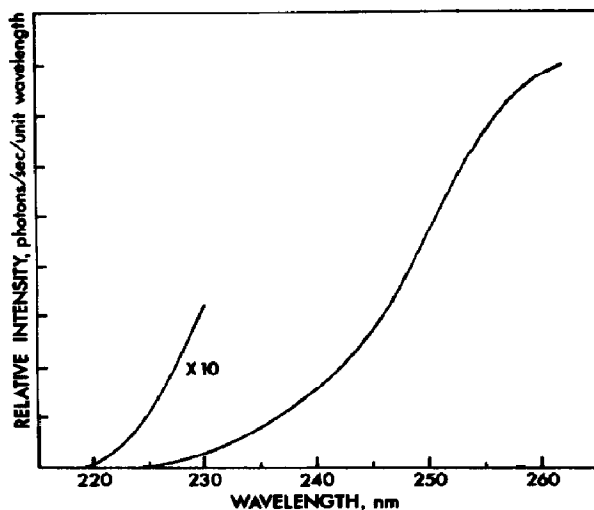
Fig. 8. Measured relative intensity of SO + O chemiluminescence.

were added downstream, including H_2O, H_2O_2, O_3, O_2, and O. Strong SO_2 chemiluminescence was observed except when O_3 was added. The intensity when oxygen atoms were added was by far the strongest. Moreover, SO_2 chemiluminescence when O atoms are added to discharged SF_6 is about 10 times more intense than SO_2 chemiluminescence formed by discharged SO_2.

Depending on the experimental conditions, many workers have found banded emission superimposed at the short wavelength onset of the SO + O recombination continuum. Higher total pressure seems to enhance the banded emission in the SO_2/inert gas system. In the SF_6 system with the various additives listed, little banded structure was observed.

The SO + O recombination continuum in units of photons/s $\times$ unit wavelength, corrected for the spectral response of the recording system, is shown in Fig. 8. Herman *et al.* [13] were unable to detect emission below 240 nm and Halstead and Thrush [12] did not find emission below 224 nm. However, we have observed emission to 218.5 ± 0.25 nm. This latter onset of the recombination continuum corresponds to a SO_2 dissociation energy of 130.85 ± 0.2 kcal/mol. The newly determined S_2 dissociation energy of 101.95 ± 0.3 kcal/mol gives the SO_2 dissociation energy of 131.2 ± 0.3 kcal/mol. These two SO_2 dissociation energies are equal within the error limits and agree well with the JANAF value of 130.97 kcal/mol [14]. Thus, SO_2 emission is produced at the predissociation limit during the SO + O recombination. This finding is in contrast to Halstead and Thrush's discussion [12]. It appears that the SO_2 α state is indeed formed in many vibrational levels. The question remains whether this is by 3 or 2 body recombination processes. It is quite likely that the SO + O recombination is very similar to the NO + O recombination where 2 and 3 body processes populate levels near the dissociation limit [15].

SO_2 photoluminescence could be easily observed at SO_2 pressures below 0.1 Torr.

Photoluminescence of CF, CF₄ and NH

Discharge products of CF_4 in helium provided sufficient amounts of the radicals CF and CF_2 to be easily observed with photoluminescence. For $CF(A^2\Sigma^+ - X^2\Pi_r)$, the (1,0), (1,1) and (0,0) bands were found near 224, 230.5 and 232.5 nm respectively; the (0,0), (0,1) and (0,2) bands of the B–X system were found at 202.5, 208 and 213.5 nm[2]. CF_2 photoluminescence was observed from 230 to 430 nm [16].

The photoluminescence at 336 nm of $NH(A^3\Pi_i - X^3\Sigma^-)$ from the discharge products of NH_3 in helium was very strong.

Acknowledgement

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