

## PHOTOCHEMISTRY OF SO<sub>2</sub> IN THE VACUUM-U.V. II. LUMINESCENCE STUDIES

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### Summary

The photolysis of SO<sub>2</sub> in H<sub>2</sub> has been studied at 147 nm (xenon line) and at 116.5 - 123.6 nm (krypton lines).

Chemiluminescent reactions of photofragments lead to the observation of the fluorescence of SO<sub>2</sub> (xenon lamp), OH(A → X) emission (xenon and krypton lamps), S<sub>2</sub>(B → X) and SO(B → X) radiative transitions (krypton lamp).

The SO(A → X) emission observed with the krypton lamp is attributed to the photodissociation of SO<sub>2</sub> at 116.5 nm (second krypton line).

The phosphorescence (a → X) of SO<sub>2</sub>, and not its fluorescence, is obtained only on irradiation with the krypton lamp and it is interpreted as the result of internal conversion from the excited state (singlet or more probably triplet) to the emitting first triplet state.

The quantum yield for SO<sub>3</sub> formation is shown to be  $\Phi \leq 0.4$  at 123.6 nm. The primary photodissociation processes giving S(<sup>1</sup>D or <sup>3</sup>P) + O<sub>2</sub> are more important with krypton lines than with the xenon line.

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### Introduction

Although much work has been devoted to the spectroscopy and fluorescence of SO<sub>2</sub>, experimental difficulties (mostly due to sulphur deposition) have inhibited the study of its photolysis.

In a preceding paper, referred to as I [1], it was shown that this deposit may at least be partly avoided when the photolysis is performed in vacuum-u.v. on mixtures of SO<sub>2</sub> and H<sub>2</sub>. However, a serious problem in the case of a molecule such as SO<sub>2</sub>, with light absorption beginning at 390 nm, is that the rare gas resonance lamps, commonly used for the vacuum-u.v. studies also emit in the near u.v.

In the first part of this paper, new results are presented on SO<sub>3</sub> formation by photolysis of SO<sub>2</sub> with a krypton lamp equipped with an interference filter centred at 123.6 nm; the second part is concerned with the luminescence observed during the photolysis.

TABLE 1  
Primary processes of SO<sub>2</sub> photodecomposition

Photodissociations	Thermodynamic thresholds (eV)	No.
SO X( <sup>3</sup> Σ <sup>-</sup> ) + O( <sup>3</sup> P)	5.5 ± 0.1	1
	O <sub>2</sub> X( <sup>3</sup> Σ <sup>-</sup> ) + S( <sup>3</sup> P)	2'
SO a( <sup>1</sup> Δ) + O( <sup>3</sup> P)	6.02	3
	O <sub>2</sub> a( <sup>1</sup> Δ <sub>g</sub> ) + S( <sup>3</sup> P)	4'
SO b( <sup>1</sup> Σ <sup>+</sup> ) + O( <sup>3</sup> P)	6.80	5
	O <sub>2</sub> X( <sup>3</sup> Σ <sup>-</sup> ) + S( <sup>1</sup> D)	6'
	O <sub>2</sub> b( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) + S( <sup>3</sup> P)	7'
SO X( <sup>3</sup> Σ <sup>-</sup> ) + O( <sup>1</sup> D)	7.46	8
	O <sub>2</sub> a( <sup>1</sup> Δ <sub>g</sub> ) + S( <sup>1</sup> D)	9'
SO a( <sup>1</sup> Δ) + O( <sup>1</sup> D)	7.98	10
	O <sub>2</sub> X( <sup>3</sup> Σ <sup>-</sup> ) + S( <sup>1</sup> S)	11'
	O <sub>2</sub> b( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) + S( <sup>1</sup> D)	12'
SO b( <sup>1</sup> Σ <sup>+</sup> ) + O( <sup>1</sup> D)	8.76	13
	O <sub>2</sub> a( <sup>1</sup> Δ <sub>g</sub> ) + S( <sup>1</sup> S)	14'
SO X( <sup>3</sup> Σ <sup>-</sup> ) + O( <sup>1</sup> S)	9.67	15
	O <sub>2</sub> b( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ) + S( <sup>1</sup> S)	16'
	O <sub>2</sub> A( <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ) + S( <sup>3</sup> P)	17'
SO a( <sup>1</sup> Δ) + O( <sup>1</sup> S)	10.21	18
SO A( <sup>3</sup> Π) + O( <sup>3</sup> P)	10.26	19
SO B( <sup>3</sup> Σ <sup>-</sup> ) + O( <sup>3</sup> P)	10.66	20
SO b( <sup>1</sup> Σ <sup>+</sup> ) + O( <sup>1</sup> S)	10.99	21
	O <sub>2</sub> A( <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ) + S( <sup>1</sup> D)	22'

### Thermodynamical data

The possible primary processes of photodecomposition, including those with multiplicity changes, which may occur during photolysis of SO<sub>2</sub> at these wavelengths are reported in Table 1. They are accompanied by their corresponding calculated thermodynamic thresholds. The dissociation energy of SO<sub>2</sub> leading to SO + O fragments has been taken as 5.5 ± 0.1 eV [2, 3]; the energies corresponding to various electronic states of SO are those of Colin [4], those corresponding to various states of O<sub>2</sub>, O and S are well known [5, 6]. The dissociation energy of SO<sub>2</sub> giving S(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sup>-</sup>) has been evaluated as 5.7 ± 0.1 eV using the values 5.3 (4) and 5.1 (15) eV for the dissociation energies of SO and O<sub>2</sub> respectively [4, 7]. Taking into account the uncertainty in the dissociation energy of SO<sub>2</sub>, the second decimal place of these energy thresholds is probably not significant; however, they are given since the energy differences between electronic states are accurately known from optical measurements.

## Spectroscopic data

### $SO(A^3\Pi \rightarrow X^3\Sigma^-)$ and $(B^3\Sigma^- \rightarrow X^3\Sigma^-)$ radiative transitions

Two electronic transitions of the radical SO have been found during the flash photolysis of COS + O<sub>2</sub> + Ar mixtures [4].

The transitions  $A_{v'} = 0,1,2,\dots,9 \rightarrow X_{v''} = 0,1$  are observed in the range 244 - 270 nm, the transition 0 → 0 being situated at 262 nm and the 1 → 0 at 259 nm. The transition ( $B^3\Sigma^- \rightarrow X^3\Sigma^-$ ) begins at 272 nm and the most intense vibrational transitions are located at 306 nm (0 → 6), 316 nm (0 → 7), 327 nm (0 → 8), 338 nm (0 → 9), 355 nm (1 → 13), 367 nm (1 → 14) [9, 10].

### $SO_2$ fluorescence and phosphorescence

When SO<sub>2</sub> is irradiated in a range of energies lying below the dissociation threshold of the molecule ( $250 < \lambda < 300$  nm), the fluorescence ( $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ ) is the sole emission observed at SO<sub>2</sub> pressures less than  $10^{-2}$  Torr [10 - 14a]; it is a continuum lying between 300 and 400 nm with a maximum at 340 nm. The phosphorescence ( $\tilde{a}^3B_1 \rightarrow \tilde{X}^1A_1$ ) appears simultaneously when the SO<sub>2</sub> pressure is increased (from  $1.3 \times 10^{-2}$  to 0.4 Torr). This phosphorescence is composed of several bands lying between 380 and 490 nm and is the sole one observed during excitation of gaseous SO<sub>2</sub> with laser radiation at 382.8 nm [14b] or when SO<sub>2</sub> is irradiated in rare gas matrices [15]. It is composed of 10 vibronic transitions from the relaxed (0-0-0) level of the excited state to vibrational levels of the ground state. It is observed that only two normal modes (symmetrical stretching frequency  $\nu_1$  and symmetrical bending frequency  $\nu_2$ ) are excited by these transitions. The antisymmetric stretching frequency  $\nu_3$  is not observed in the phosphorescence of SO<sub>2</sub>.

The ratio of phosphorescence to fluorescence  $\Phi_P/\Phi_F$ , increases with pressure at a given exciting wavelength (at  $\lambda_{exc} = 265$  nm,  $\Phi_P/\Phi_F$  varied from 0.1 at  $P_{SO_2} = 1.3 \times 10^{-2}$  Torr to 0.5 at  $P_{SO_2} = 0.2$  Torr).

For a given pressure,  $\Phi_P/\Phi_F$  rapidly decreases as one goes to shorter exciting wavelengths. These variations in the  $\Phi_P/\Phi_F$  ratio have been attributed to competition between fluorescence and a bimolecular intersystem crossing from the lower vibrational levels of the  $\tilde{A}$  state formed by internal conversion. The bimolecular intersystem crossing leads to the triplet manifold,  $\tilde{a}$ , which after vibrational relaxation phosphoresces.

Two different groups of rovibronic states having different lifetimes have been observed recently [16] by studies of the time resolved fluorescence of SO<sub>2</sub>; the long lifetime states ( $80 < \tau_{\mu s} < 600$ ) could be responsible for the bimolecular intersystem crossing leading to the triplet manifold.

It can be noted, however, that no fluorescence was observed when the exciting wavelength is less than 220 nm; this has been attributed to the predissociation of SO<sub>2</sub> at this wavelength [13].

### *Chemiluminescence involving SO<sub>2</sub>*

The spectral distribution of chemiluminescence produced by microwave discharges in SO<sub>2</sub> is dependent on the gas pressure and the discharge intensity [17]. At low pressures and with a strong discharge, atomic lines of S and O are observed; a less intense discharge leads [18] to the observation of two transitions (A → X and B → X) of the SO radical described above. When the SO<sub>2</sub> pressure is increased, the spectral distribution is different [17, 19]; it is a continuous emission between 230 and 490 nm with 3 maxima at 275, 340 and 440 nm. The two last maxima were readily attributed to the fluorescence  $\tilde{A} \rightarrow \tilde{X}$  and the phosphorescence  $\tilde{a} \rightarrow \tilde{X}$  of SO<sub>2</sub> but the maximum at 275 nm was more difficult to identify; it could be attributed either to the transition SO(A<sup>3</sup>Π → X<sup>3</sup>Σ<sup>-</sup>) or to a radiative transition from the second singlet excited state of SO<sub>2</sub>( $\tilde{B}^1A_1$ ) [19, 20].

The same spectral distribution is also observed in explosions of SO<sub>2</sub> + O<sub>2</sub>, CS<sub>2</sub> + O<sub>2</sub>, COS + O<sub>2</sub> mixtures [21].

When an H<sub>2</sub>S + O<sub>2</sub> mixture is irradiated by flash photolysis [22] or passed through an electrical discharge [23], the chemiluminescence is composed of the following emissions:

On the continuum from 230 to 490 nm described above, are superimposed bands of the (B<sup>2</sup>Σ<sub>u</sub> → X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) system of S<sub>2</sub>, the strongest being those with  $v' = 6, 7, 8, 9$  [24, 25]. Bands of the (B<sup>3</sup>Σ<sup>-</sup> → X<sup>3</sup>Σ<sup>-</sup>) system of SO are also observed, the strongest being those with  $v' = 8, 9, 10$ . These emissions could arise from chemiluminescent recombinations S + S + M → S<sub>2</sub><sup>\*</sup> + M and S + O + M → SO<sup>\*</sup> + M. These possibilities are supported by the correlations suggested by Colin [4, 26] between: (a) SO(B<sup>3</sup>Σ<sup>-</sup>) and S(<sup>1</sup>D) + O(<sup>3</sup>P); (b) SO(A<sup>3</sup>π) and S(<sup>3</sup>P) + O(<sup>3</sup>P); (c) S<sup>2</sup>(B<sup>3</sup>Σ<sub>u</sub>) and S(<sup>3</sup>P) + S(<sup>1</sup>D).

## Experimental

### *Quantum yields of SO<sub>3</sub>*

The experimental apparatus is the same as that used previously [1]. Gaseous mixtures are admitted continuously to the reaction vessel with a greaseless and mercury free flow system with flow rates close to 100 cm<sup>3</sup>/s and total pressures between 3 and 100 Torr. We have observed that although it was difficult to eliminate completely air leaks into the system when it was used statically, there was no problem with leaks when the flow system was used. The r.f. powered krypton resonance lamp is equipped with a titanium getter to remove the impurities in the lamp. The emission spectrum of the lamp is periodically tested with a vacuum u.v. monochromator (Coderg M.S. 102) having a grating 2400 lines/mm blazed at 123.6 nm; when the lamp is sealed with a LiF window, the 123.6 nm line is seven times more intense than the 116.5 nm line and an important part of the emission is composed of near u.v. lines ( $\lambda > 300$  nm).

To eliminate this part of the spectrum, an interference filter centred at 123.6 nm is used instead of a LiF window. This filter (Seavom) is made

of aluminium evaporated under vacuum onto a LiF window and has a transmission of 17% at 123.6 nm; the emission spectrum of the lamp is then reduced essentially to this line alone and the intensity as measured by NO photoionization is close to  $10^{14}$  photons/s in the reaction vessel. This value is five times smaller than when the lamp is sealed with the LiF window so that, because of limitations of the titrimetric method used to measure  $\text{SO}_3$  [1], irradiation times had to be increased appreciably.

### Luminescence studies

For the luminescence studies, the cell was modified to allow observation of the emission at right angles to the incident radiation. The blackened Pyrex bulb is equipped with two Wood's horns to eliminate the scattered light emitted in the visible and u.v. range by the lamp (Fig. 1).

The experiments were performed at krypton and xenon resonance wavelengths, using the lamps sealed with LiF windows. The luminescence quantum yields are so small that the interference filter could not be used.

The light emission in the spectral range 300 - 600 nm was analyzed by a monochromator, Coderg MS 102, having a grating 1830 lines/mm blazed at 500 nm. The photomultiplier, a selected Hamamatsu R. 212 UHS, is sensitive in the spectral range 250 - 650 nm and was connected to a picoammeter (Lemouzy Tekelec P.A. 15 T). Its output was recorded with a Graphirac Sefram recorder. The photomultiplier noise was equal to  $10^{-11}$  A (*i.e.*  $10^{-17}$  A at the photocathode) so that the lowest acceptable signal was  $2 \times 10^{-11}$  A.

In the spectral range, 400 - 910 nm, the emission was observed using the monochromator equipped with another grating, 1221 lines/mm, blazed at 750 nm; the photomultiplier, Hamamatsu R 666 cooled at  $-20^\circ\text{C}$ , is five times less sensitive than the previous one.

The luminescence intensity is so weak that the spectra were scanned with slitwidth of 2 mm corresponding to a resolution of about 30 Å.

The absorption coefficient of  $\text{SO}_2$  at the xenon resonance wavelength (147 nm) is  $100\text{ cm}^{-1}\text{ atm}^{-1}$ . It is higher at the krypton wavelengths:

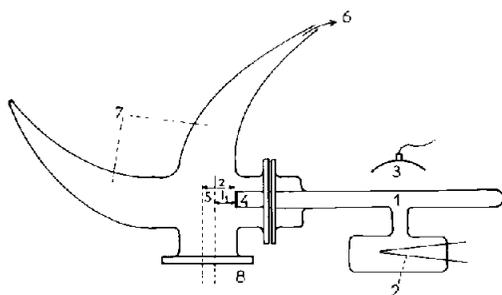


Fig. 1. Experimental apparatus. 1, Lamp; 2, titanium wires; 3, microwave power antenna; 4, LiF window; 5, gas input and pressure measurements in the photolysis cell; 6, gas output and vacuum; 7, Wood's horns; 8, observation quartz window.

$\epsilon = 200 \text{ cm}^{-1} \text{ atm}^{-1}$  at 116.5 nm;  $\epsilon = 1000 \text{ cm}^{-1} \text{ atm}^{-1}$  at 123.6 nm [27]. The  $\text{SO}_2$  pressure corresponding to a maximum in the intensity of the detected luminescence,  $P_{\text{max}}$ , is related to the absorption coefficient and to the viewing region geometry by the formula:

$$P_{\text{max}} = \ln(l_2/l_1)/(l_2 - l_1)\epsilon$$

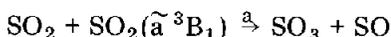
$l_1$  and  $l_2$  being the distances between the lamp window and viewing region boundaries. This formula gives at 147 nm:  $P_{\text{max}} = 3 \pm 2$  Torr and at 123.6 nm:  $P_{\text{max}} = (3 \pm 2) \times 10^{-1}$  Torr.

## Results

### *Quantum yields for $\text{SO}_3$ formation*

The irradiations were performed in mixtures of 1%  $\text{SO}_2$  in  $\text{H}_2$ . The value of the quantum yield for the formation of  $\text{SO}_3$  from the  $\text{SO}_2$  photolysis at 123.6 nm, is  $\Phi \leq 0.4$  for  $P_{\text{SO}_2}$  of 0.4 Torr,  $P_{\text{H}_2}$  of 90 Torr, a flow rate of  $150 \text{ cm}^3/\text{s}$  and an irradiation time of 240 min. This value is much lower than that found previously [1] with a krypton lamp without an interference filter (between 6 and 10 times under similar conditions).

This result correlates with the diminution in yields observed previously [1] when a quartz window was used in place of a LiF window. Consequently, a part of the  $\text{SO}_3$  formation at longer wavelengths can be explained by the following step, first postulated by Calvert and Coll [14a]:



As it will be shown later, the  $\text{SO}_2$  photolysis at the wavelength of the krypton lines leads to formation of sulphur and oxygen atoms, oxygen molecules and SO radicals (in excited electronic states or not) and also to  $\text{SO}_2$  molecules in the  $\tilde{\text{a}}^3\text{B}_1$  state. It follows that the  $\text{SO}_3$  formation may result from any reaction involving these species; this displays the limitation of a photochemical study using a stable reaction product as the measured parameter.

### *Luminescence studies*

The irradiations were again performed in mixtures of  $\text{SO}_2$  and  $\text{H}_2$ . The danger of sulphur deposition on the lamp window limits the range of concentrations available.

With the xenon lamp it is possible to vary the  $\text{SO}_2/\text{H}_2$  ratio between 1 and 10%. With the krypton lamp, one could only work with up to 1%  $\text{SO}_2$  in  $\text{H}_2$ .

The experimental results are divided into three parts. The first is concerned with results common to both lamps; the second and third parts describe results peculiar to each lamp.

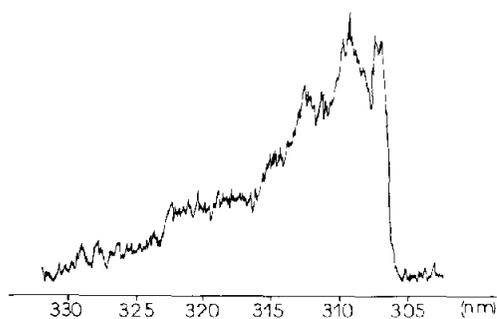
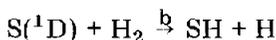


Fig. 2. Emission spectrum of  $\text{OH}(A^2\Sigma^+ \rightarrow X^2\pi)$  formed during the photolysis of  $\text{SO}_2$  at krypton lines with  $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr,  $P_{\text{H}_2} = 0.5$  Torr.

*Common results for xenon and krypton lamps: OH ( $A^2\Sigma^+$ ) emission*

At low  $\text{SO}_2$  pressures well below the best detection pressure for the luminescence, cutting off the gas flow to the cell during the photolysis leads to the appearance of an emission whose intensity grows with time; for an irradiation time of 15 min, its intensity increases by a factor of 2 for the xenon lamp, and by a factor of 100 for the krypton lamp. In the latter case (Fig. 2), the spectrum of this emission has been analyzed between 306.4 and 330 nm and can be attributed to the  $\text{OH}(A^2\Sigma_{v'=0}^+ \rightarrow X^2\pi_{v''=0})$  transition.

As the rotational distribution of this emission is different from emissions observed during  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$  photolyses [28, 29], the emission cannot result from a secondary photolysis of these compounds. On the other hand, we think that it is related to air contamination since it only appears with the static system. It is suggested that the following reaction:  $\text{H} + \text{O}_2 + \text{H}_2 \xrightarrow{\text{h}\nu} \text{OH}^* + \text{H}_2\text{O}$ , in which the exothermicity is high enough to produce OH in the  $^2\Sigma^+$  state, occurs here, H atoms being formed by the previously [1] postulated reaction:



The reaction (c) has been postulated [30] to explain the origin of OH luminescence during the induction period of the  $\text{H}_2 + \text{O}_2$  reaction behind shock-waves. Since the OH emission is more intense by a factor of 50 with the krypton lamp than with the xenon lamp (the relative intensities of which are in just the reverse order) one can infer that the photodissociation process  $\text{S}(^1\text{D}) + \text{O}_2$  is more important at 123.6 and 116.5 nm than at 147 nm.

We have carefully looked for light emission corresponding to the excited states of oxygen atoms and molecules. The  $\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})$  transition at 630 nm was not detected. The  $\text{O}(^1\text{S}) \rightarrow \text{O}(^1\text{D})$  transition cannot be obtained by irradiation with the xenon lamp (see Table 1); in the krypton lamp it is hidden by a krypton line. The  $\text{O}_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$  transition has not been observed with the xenon lamp; again it is hidden with the krypton lamp by krypton lines. The  $\text{O}_2(A^3\Pi \rightarrow X^3\Sigma^-)$  Herzberg bands, which can only occur with the krypton lamp, have not been detected.

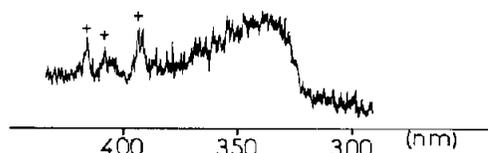


Fig. 3. Fluorescence of  $\text{SO}_2(\tilde{A}^1B_1)$  formed during the photolysis of  $\text{SO}_2$  at 147 nm with  $P_{\text{SO}_2} = 15$  Torr,  $P_{\text{H}_2} = 90$  Torr and a flow rate  $D = 60 \text{ cm}^3/\text{s}$ . + designates Xe scattered lines.

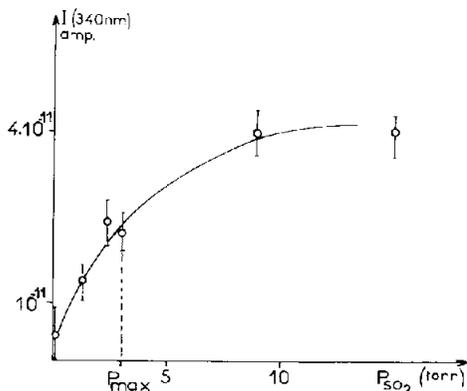


Fig. 4. Fluorescence intensity at  $\lambda = 340 \text{ nm}$  as a function of the  $\text{SO}_2$  pressure during the photolysis of  $\text{SO}_2$  with xenon lamp.

#### Irradiation at 147 nm

At  $\text{SO}_2$  pressures higher than  $10^{-1}$  Torr, a luminescence appears as a band extending from 325 to 388 nm with a maximum at 340 nm (Fig. 3). This emission can be attributed to  $\text{SO}_2$  fluorescence ( $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ ). Its intensity is independent of  $\text{H}_2$  pressure but increases as the  $\text{SO}_2$  pressure is increased up to values higher than those previously calculated for the best detection of luminescence (Fig. 4).

The phosphorescence of  $\text{SO}_2(\tilde{a}^3B_1 \rightarrow \tilde{X}^1A_1)$  was not detected.

#### Irradiation at 116.5 nm and 123.6 nm

Three kinds of emission have been observed which are most intense at very low  $\text{SO}_2$  pressures ( $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr). Their intensity decreases with increasing  $\text{SO}_2$  pressures before the optimum value previously calculated is reached ( $3 \times 10^{-1}$  Torr). Their relative intensities are dependent on the  $\text{SO}_2$  pressure and on the flow rate.

(A) The first emission, the phosphorescence of  $\text{SO}_2(\tilde{a}^3B_1)$  is the most intense one at low pressures. As the  $\text{SO}_2$  is increased to  $P_{\text{SO}_2} = 10^{-1}$  Torr, the emission disappears (Figs. 5a and b); on the other hand, its intensity increases with decreasing flow rate. As is shown by Fig. 6, 9 vibronic transitions have been identified at  $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr. The emission lines of the krypton lamp cover the spectral range between 423 nm and 450 nm where the most intense bands of the phosphorescence are located.

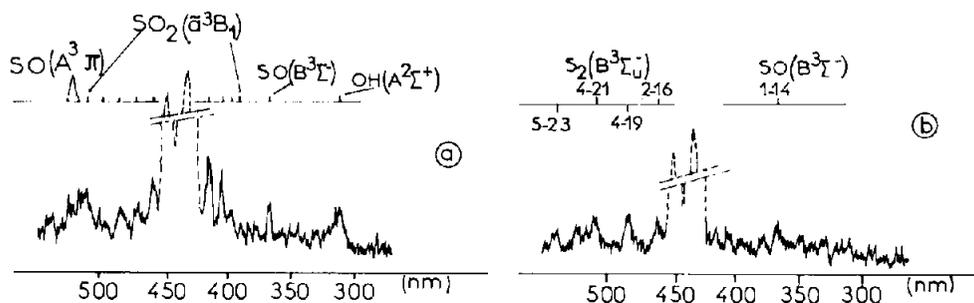


Fig. 5. Luminescence observed during the photolysis of  $\text{SO}_2$  at krypton lines. (a) with  $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr,  $P_{\text{H}_2} = 0.5$  Torr, and  $D = 5 \text{ cm}^3/\text{s}$ ; (b) with  $P_{\text{SO}_2} = 0.1$  Torr,  $P_{\text{H}_2} = 10$  Torr and  $D = 100 \text{ cm}^3/\text{s}$ . ---- are lines from the lamp.

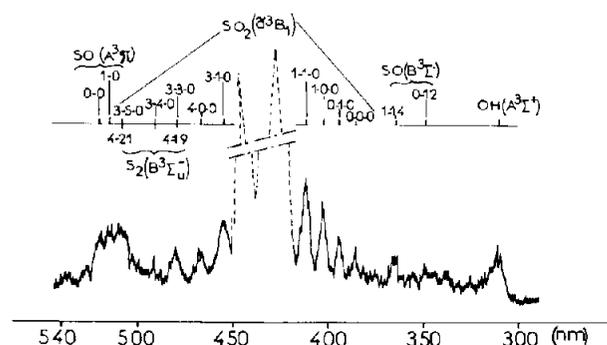


Fig. 6. Luminescence observed during photolysis of  $\text{SO}_2$  at the krypton lines with  $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr,  $P_{\text{H}_2} = 0.5$  Torr and a flow rate close to  $10 \text{ cm}^3/\text{s}$ . --- are lines from the lamp.

The vibrational assignments have been calculated taking  $\nu_1 = 1147 \text{ cm}^{-1}$  and  $\nu_2 = 517 \text{ cm}^{-1}$  [15] and are presented in Table 2. The difference between the observed and calculated values is never more than  $100 \text{ cm}^{-1}$ , this value corresponding to the error in the determination of the band maxima. These transitions originate from the relaxed  $0-0-0 \tilde{a}$  state.

(B) The second emission consists of the two transitions, ( $\text{A}^3\Pi \rightarrow \text{X}^3\Sigma^-$ ) and ( $\text{B}^3\Sigma^- \rightarrow \text{X}^3\Sigma^-$ ) of the SO radical, which are observed at  $P_{\text{SO}_2} = 6 \times 10^{-3}$  Torr (Fig. 6).

The  $\text{A} \rightarrow \text{X}$  transition is more intense than the  $\text{B} \rightarrow \text{X}$  transition; it is observed in the second order at 522 and 517 nm. The second  $\text{B} \rightarrow \text{X}$  transition is characterized by a line at 367 nm and a second one, very weak, at 351 nm. The vibrational assignments are given in Table 3. If the  $\text{SO}_2$  pressure is increased to  $P_{\text{SO}_2} = 10^{-1}$  Torr, the emission disappears (Figs. 5a and b).

TABLE 2

Transition of  $\text{SO}_2(\tilde{a}^3\text{B}_1 \rightarrow \tilde{\text{X}}^1\text{A}_1)$ 

$v'$			$v''$			$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	$\Delta(\nu_{v'} - \nu_{v''})(\text{cm}^{-1})$	
$\nu_1$	$\nu_2$	$\nu_3$	$\nu_1$	$\nu_2$	$\nu_3$			observed	calculated
0	0	0	0	0	0	389	25700	27	0
"	"	"	0	1	0	398	25120	607	517
"	"	"	1	0	0	407	24570	1157	1147
"	"	"	1	1	0	416	24030	1697	1664
"	"	"	3	1	0	459	21780	3947	3958
"	"	"	4	0	0	472	21180	4547	4588
"	"	"	3	2	0				4475
"	"	"	3	3	0	484	20660	5067	4992
"	"	"	2	5	0				4879
"	"	"	3	4	0	496	20160	5567	5509
"	"	"	3	5	0	510	19600	6127	6026

TABLE 3

Transitions of the SO radical

$\text{A}^3\pi \rightarrow \text{X}^3\Sigma^-$		$\text{B}^3\Sigma^- \rightarrow \text{X}^3\Sigma^-$	
$v' - v''$	$\lambda(\text{nm})$	$v' - v''$	$\lambda(\text{nm})$
0 - 0	261	0 - 12	351
1 - 0	258	1 - 14	367

TABLE 4

Transition of  $\text{S}_2(\text{B}^3\Sigma_u^- \rightarrow \text{X}^3\Sigma_g^-)$ 

(nm)	$v' - v''$
459	2 - 16
484	4 - 19
510	4 - 21
538	5 - 23

TABLE 5

Summary of results

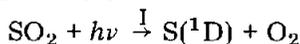
Transitions	$P_{\text{SO}_2}(\text{Torr})$	$P_{\text{H}_2}(\text{Torr})$	$D(\text{cm}^2/\text{s})$	$\lambda_{\text{exc.}}(\text{nm})$
$\text{SO}_2(\tilde{\text{A}}^1\text{B}_1 \rightarrow \tilde{\text{X}}^1\text{A}_1)$	$10^{-1} < P < 30$	$5 \times 10^{-1} < P < 170$	$40 < D < 100$	147
$\text{OH}(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$	$10^{-2}$	$10^{-1}$	0	147
$\text{SO}_2(\tilde{a}^3\text{B}_1 \rightarrow \tilde{\text{X}}^1\text{A}_1)$	$6 \times 10^{-3} < P < 6 \times 10^{-2}$	$5 \times 10^{-1} < P < 10$	$20 < D < 40$	123.6 - 116.5
$\text{SO}(\text{A}^3\Pi \rightarrow \text{X}^3\Sigma^-)$	$6 \times 10^{-3} < P < 6 \times 10^{-2}$	$5 \times 10^{-1} < P < 10$	$20 < D < 40$	123.6 - 116.5
$\text{SO}(\text{B}^3\Sigma^- \rightarrow \text{X}^3\Sigma^-)$	$6 \times 10^{-3} < P < 10^{-1}$	$5 \times 10^{-1} < P < 20$	$20 < D < 40$	123.6 - 116.5
$\text{S}_2(\text{B}^3\Sigma_u^- \rightarrow \text{X}^3\Sigma_g^-)$	$6 \times 10^{-2} < P < 10^{-1}$	$5 \times 10^{-1} < P < 20$	$20 < D < 40$	123.6 - 116.5
$\text{OH}(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$	$6 \times 10^{-3}$	$5 \times 10^{-1}$	0	123.6 - 116.5

(C) The third emission is attributed to the transition ( $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ ) of  $S_2$  which is observed at higher  $SO_2$  pressures ( $10^{-1}$  Torr) when the  $SO_2$  phosphorescence has diminished. At low pressures, the  $S_2$  emission is obscured by the  $SO_2$  phosphorescence and we cannot say whether it occurs (Fig. 5b). The vibrational assignments are reported in Table 4.

A summary of the results is given in Table 5. It is worthwhile noting that none of the emissions observed can be attributed to a contribution from the visible and near u.v. lines of the exciting radiation since, this part of the spectrum being analogous in the two lamps, one would expect identical effects.

## Discussion

The result for the excited state of OH clearly indicates the occurrence of a primary process:

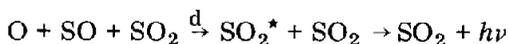


followed by  $S(^1D) + H_2 \xrightarrow{b} SH + H$

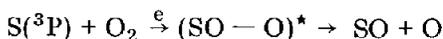
This process (I) has a higher quantum yield at shorter exciting wavelengths. A similar conclusion may be drawn from the effect of concentration on sulphur deposition about the photodissociation process  $SO_2 + h\nu \xrightarrow{II} S(^3P) + O_2$ .

### Irradiation at 147 nm

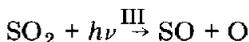
The fluorescence of  $SO_2(\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1)$  observed at 147 nm has the features of a collision induced-emission (Fig. 4) rather than an emission from the original excited molecule. It seems likely that the chemiluminescent reaction is:



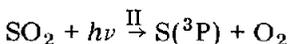
The species SO and O are not necessarily the primary photofragments produced by a dissociation process which competes with the photodissociation reactions (I) and (II); it is shown that the recombination  $S(^3P) + O_2$  leads to a short lived transition state ( $\tau < 10^{-10}$  s) which dissociates giving SO + O [31]:



The reaction (d) could be preceded by reaction (e) and it is not possible to establish whether the observed fluorescence results from photodissociation



or



The chemiluminescence produced by reaction (d) has the same features as the  $SO_2$  luminescence produced by photonic excitation at  $230 < \lambda \text{ nm} < 260$  where phosphorescence does not occur [12].

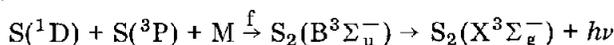
It follows that high vibrational levels of the first excited singlet state of  $\text{SO}_2$  are populated by  $\text{O} + \text{SO}$  recombination (reaction d): one or both of those photofragments must then be in an energy rich state.

*Irradiation at 123.6 and 116.5 nm*

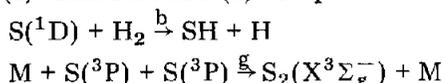
*Chemiluminescence*

Two chemiluminescences are observed, one from  $\text{S}_2(\text{B}^3\Sigma_u^-)$  and one from  $\text{SO}(\text{A}^3\Pi)$  and  $\text{B}^3\Sigma$ .

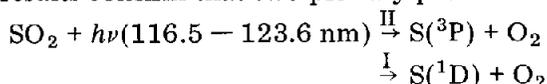
The  $\text{S}_2(\text{B}^3\Sigma_u^-)$  is formed in its higher vibrational levels from  $\text{S}(\text{D}^1)$  and  $\text{S}(\text{P}^3)$  with which it correlates:



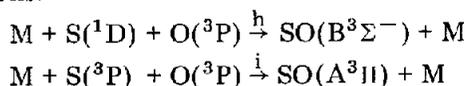
The presence of a sulphur deposit and the partial inhibition of the formation of the deposit by  $\text{H}_2$  indicates that both  $\text{S}(\text{P}^3)$  and  $\text{S}(\text{D}^1)$  are present in reaction (f). This reaction (f) competes with:



The results confirm that two primary processes occur at these wavelengths:



It is possible that the  $\text{O}_2$  molecules may be excited (reactions 4' - 7' - 17' in Table 1) but the corresponding radiative transitions were not observed perhaps owing to their quenching by  $\text{H}_2$  present in the system. The formation of the  $\text{SO}$  excited states A and B can be explained also by atomic recombinations:

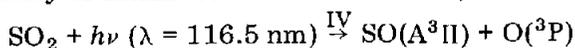


Reaction (h) is exothermic enough to give the vibrational level  $v = 1$  of  $\text{SO}(\text{B}^3\Sigma^-)$ .

*Excited photofragment*

The luminescence from  $\text{SO}(\text{A}^3\Pi)$  is more intense than that from  $\text{SO}(\text{B}^3\Sigma^-)$  at lower pressures. It is then possible that this species does not originate solely from reaction (i).

Only at 116.5 nm (10.64 eV) can the photolysis of  $\text{SO}_2$  lead to the photofragment  $\text{SO}(\text{A}^3\Pi)$ . As it can be seen from Table 1, the dissociation channel 19 leading to  $\text{SO}(\text{A}^3\Pi)_{v=0}$  has an energy of 10.26 eV (10.36 eV is necessary to attain vibrational level  $V = 1$ ):

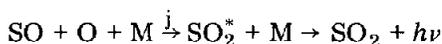


This reaction may not be the only source of  $\text{O}(\text{P}^3)$  which is required for the chemiluminescent reactions (h) and (i).

It is evident that  $\text{SO}(\text{B}^3\Sigma^-)$  cannot be formed by a direct photodissociation. It can be seen from Table 1 that 10.66 eV is necessary to dissociate the molecule by reaction (20); to produce  $\text{SO}(\text{B}^3\Sigma^-)$  in the vibrational level  $v = 1$ , the corresponding energy is 10.74 eV. This value is too high even when the uncertainty of the thermodynamic data is taken into account.

*Phosphorescence of  $\text{SO}_2(\tilde{a}^3\text{B}_1 \rightarrow \tilde{\text{X}}^1\text{A}_1)$*

This radiative transition cannot be due to chemiluminescence such as:



because it is observed at very low  $\text{SO}_2$  pressures where the fluorescence would be observed more readily than the phosphorescence (which is induced by collision).

It seems likely that phosphorescence of  $\text{SO}_2$  is an emission from the original excited molecule.

The states of  $\text{SO}_2$  excited at 116.5 and 123.6 nm are not well known although the successive members of a Rydberg series have been identified in the absorption spectrum, together with valence transitions [2, 32]. Photonic absorption may lead to excitation of a singlet manifold level or to direct excitation of a triplet manifold level.

In the first case, one must suppose that the excited state relaxes in a rovibronic group which is not predissociated. The singlet state vibrational level attained is necessarily long-lived to allow a bimolecular intersystem crossing. Even though one supposes that this state is a high vibrational level of the group having a lifetime equal to 60  $\mu\text{s}$  which makes a minor contribution to the fluorescence emission at low excitation energy [16], the complete absence of fluorescence cannot be explained.

So, the most probable explanation for the observed phosphorescence is a mechanism with a direct excitation of a triplet electronic level which is allowed because of the strong spin orbit coupling and the mixing of rovibronic states of  $\text{SO}_2$  at these energies. A vibrational relaxation of 7 eV leads to population of the 0-0-0 level of the ( $\tilde{a}^3\text{B}_1$ ) state of the triplet manifold. The presence of  $\text{H}_2$  probably facilitates this relaxation, which is then followed by the phosphorescence.

Nevertheless, it is worthwhile noting that the fact that no phosphorescence appears when the exciting wavelength is 147 nm may not be interpreted as proof that the triplet manifold is not populated at this wavelength. As the absorption coefficient at 147 nm is ten times smaller than at 123.6 nm, a similar light absorption will be obtained with a ten times higher  $\text{SO}_2$  pressure where self-quenching of the phosphorescence will occur.

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