TWO-PHOTON UV EXCITATION OF SO_2 AND LASER-INDUCED FLUORESCENCE FROM SO

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Summary

Strong fluorescence from $SO(B\ ^3\Sigma^-\ (v' = 2) \rightarrow X\ ^3\Sigma^-\ (v'' = n))$ has been observed following KrF laser (248 nm) excitation of SO_2. The SO radicals are initially formed in their ground electronic state by a sequential two-photon absorption mechanism involving the $\tilde{B}\ ^1B_1$ state of SO_2 as an intermediate state and a high-lying Rydberg state as the dissociative state. The SO radicals then absorb a further photon at 248 nm which gives rise to the observed SO(B–X) fluorescence.

1. Introduction

UV multiphoton excitation of small molecules provides a convenient means of producing a wide variety of excited state species [1 - 4]. As the chemical behaviour of these excited states is frequently very different from that of the ground state their study is of considerable fundamental importance [5]. In the present work we show that SO radicals can be produced in a single vibrational level of the B $^3\Sigma^-$ state by two-photon dissociative excitation of SO_2 followed by single-photon excitation of the SO radical using a KrF laser (248 nm).

A preliminary report on the two-photon excitation of SO_2 has been given previously [6]. It was shown that SO_2 can be pumped by a sequential two-photon mechanism to a high-lying Rydberg state which dissociates to form an oxygen atom and an SO radical. The SO radical was found to absorb a further photon from the same laser pulse and thus gives rise to an intense laser-induced fluorescence spectrum. In the work presented here higher resolution spectra of the SO fluorescence have been obtained and as a result

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the assignment of the transition is revised. While this paper was in the final stages of preparation a further paper on the two-photon excitation of SO_2 appeared [7]; however, the main emphasis in that work was placed on the observation of emission from atomic sulphur. In our work emphasis is placed on laser-induced fluorescence from the SO radical and the spectra presented are more detailed than those given in previous work.

2. Experimental details

A general description of the experimental arrangement employed here for observing photofragment fluorescence following laser excitation has been given elsewhere [1, 8]. Two different KrF lasers were employed: the first was a Lambda Physik EMG500 excimer laser giving pulse energies of about 20 mJ (pulse duration, 18 ns); the second was a Lambda Physik EMG201 laser delivering 300 mJ (pulse duration, 15 ns). In the experiments with the first laser the output was tightly focused by using a combination of a cylindrical and a convex lens. Photofragment fluorescence was observed at right angles and dispersed by means of a Jobin–Yvon HRS 2 monochromator with a resolution of 0.7 Å. In the experiments with the second laser focusing was less tight and the second-order spectra were recorded with a resolution of 1 Å using a Monospek 500 monochromator (the grating was blazed for 700 nm in first order). An EMI 9781B photomultiplier tube (modified S5 response) was used with both monochromators. The spectra were recorded over the range 250 - 450 nm. The spectral response of the first detection system (combination of the Jobin–Yvon monochromator and the photomultiplier) was obtained by using a Glen Creston Instruments halogen–tungsten standard lamp of known spectral irradiance. The response was found to be fairly flat over the region of interest, with wavelengths at about 270 nm being favoured by a factor of 1.5 over those at about 380 nm.

The SO_2 samples (BDH Chemicals) were thoroughly degassed before use in a vacuum line capable of maintaining a vacuum of better than 10^{-4} N m^{-2}. The pressures were measured using an MKS Baratron.

3. Results and discussion

The excitation of SO_2 using low KrF laser intensities (4 MW cm^{-2}) gives rise to a broad featureless fluorescence spectrum in the region 250 - 430 nm. This fluorescence is readily assigned to the well-known $SO_2(\tilde{B}\ ^1B_1 \rightarrow \tilde{X}\ ^1A_1)$ transition, and it appears to be featureless under our excitation conditions because of the large number of rovibronic states excited by the relatively broad band output of the KrF laser ($\Delta\lambda \approx 0.5$ nm).

At higher laser intensities (40 MW cm^{-2} and above) sharp spectral features are superimposed on the broad fluorescence discussed above (Figs. 1 and 2). These sharper features are readily assigned to SO radical fluorescence as their spacing corresponds well to a progression in the ground electronic state.
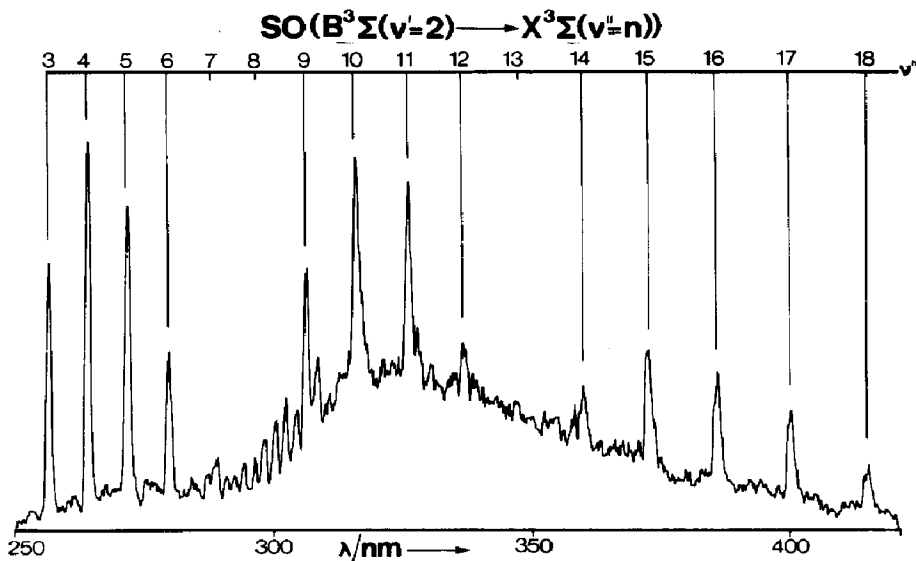
$$SO(B^3\Sigma(v'=2) \longrightarrow X^3\Sigma(v''=n))$$

Fig. 1. Fluorescence observed following excitation of SO_2 ($P = 1.3$ kN m^{-2}) at 248 nm with the focused output of a KrF laser. The sharp SO(B $^3\Sigma^-$ (v' = 2) → X $^3\Sigma^-$ (v'' = n)) fluorescence is superimposed on the broader fluorescence from $SO_2(\tilde{B}\,^1B_1 \to \tilde{X}\,^1A_1)$. The spectrum has not been corrected for the response of the detection system.

$$SO(B^3\Sigma(v'=2) \longrightarrow X^3\Sigma(v''=n))$$
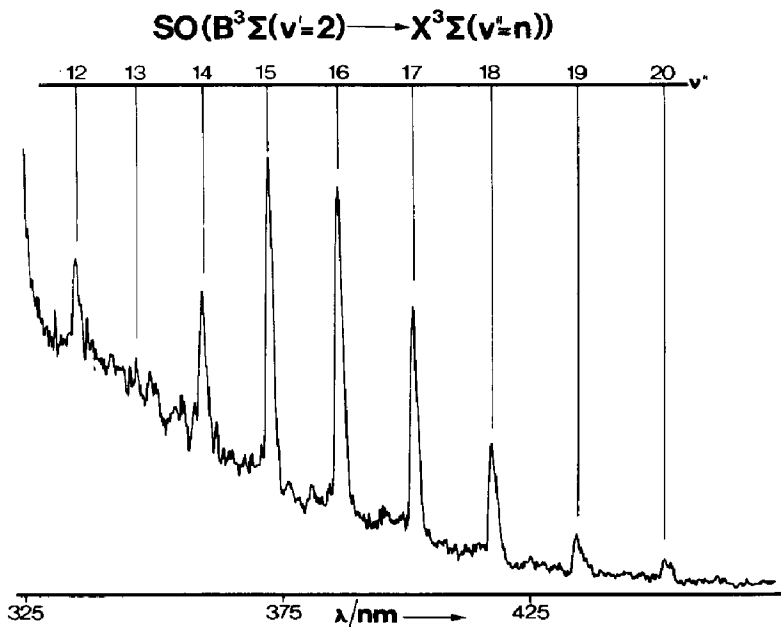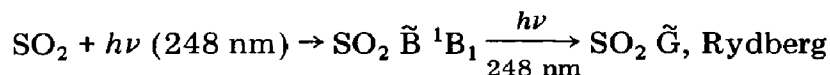
Fig. 2. Expansion of the long wavelength section of SO(B $^3\Sigma^-$ (v' = 2) → X $^3\Sigma^-$ (v'' = n)) fluorescence (conditions as for Fig. 1).

The mechanism by which the SO radical is formed has been described by Fotakis [6] and will be only briefly outlined here. Sequential two-photon excitation of SO_2 via the $\tilde{B}\,^1B_1$ state populates the high-lying $\tilde{G}$ Rydberg state:

$$SO_2 + h\nu \text{ (248 nm)} \rightarrow SO_2 \, \tilde{B} \, {}^1B_1 \xrightarrow[\text{248 nm}]{h\nu} SO_2 \, \tilde{G}, \text{ Rydberg}$$

Spectroscopic studies by Dujardin and Leach [9] have shown that the $\tilde{G}$ state is predissociated and thus can give rise to SO radicals. There is considerable excess energy available in this dissociation process for partitioning between the photofragments (see ref. 10 for a full list of possible processes). SO can be formed in one of its low-lying electronic states (*i.e.* a ${}^1\Delta$ or b ${}^1\Sigma$ states) or with quite high levels of vibrational excitation in its ground electronic state. More detailed studies will be required to characterize fully the energy partitioning in the dissociation of the $\tilde{G}$ state of SO_2, but for the present purposes we note that it is not possible, on energetic grounds, to produce directly either SO A ${}^3\Pi_i$ or SO B ${}^3\Sigma^-$. Thus the observed fluorescence must result from the absorption of a further photon by either SO_2 or the SO radical. The absorption of a third photon by SO_2 would carry the molecule above its first ionization limit, and although it is possible to produce substantial yields of excited state photofragments above this limit we would not expect to observe such a simple fluorescence spectrum as photodissociation normally leads to a relatively broad spread of vibrational quantum states. The observed fluorescence can be fully accounted for in terms of a progression from a single vibrational level of an upper electronic state.

In previous work this fluorescence was attributed to emission from the A ${}^3\Pi_i$ state of SO. The relatively low resolution attainable in those experiments did not allow an unambiguous assignment of the upper state, and the assignment was based on suggestions made by Clyne and coworkers [11, 12] that optical pumping of this state by KrF laser radiation should be favourable. The improvement in resolution in the present work, together with the observation of fluorescence at longer wavelengths, now allows a definite assignment.

It is clear that the bands shown in Figs. 1 and 2 eliminate all but one of the possible progressions which can originate from the A ${}^3\Pi_i$ state [6], the remaining possibility being the A ${}^3\Pi_2$ ($v' = 11$) $\rightarrow$ X ${}^3\Sigma$ ($v'' = n$) progression. Alternatively these bands can be assigned to a progression from the $v' = 2$ level of the B ${}^3\Sigma^-$ state. Both the A ${}^3\Pi_2$ ($v' = 11$) and the B ${}^3\Sigma^-$ ($v' = 2$) states can be excited from the $v'' = 2$ level of SO X ${}^3\Sigma^-$ at 248 nm. The Franck–Condon factors for a progression originating from SO B ${}^3\Sigma^-$ ($v' = 2$) are consistent [13] with the relative intensities (corrected for detector and monochromator response) of the observed bands. The Franck–Condon factors for transitions from the A ${}^3\Pi_2$ ($v' = 11$) level are not known but it is clear from the overall envelope of intensity that this is consistent with transitions from a level with $v' = 2$ rather than $v' = 11$ (*i.e.* three broad oscillations are observed rather than twelve). Furthermore a comparison of the radiative lifetimes for the A ${}^3\Pi_i$ and B ${}^3\Sigma^-$ states shows that absorption to the latter should be approximately one or two orders of magnitude more intense than that to the former. We therefore expect the B ${}^3\Sigma^-$ state to be

populated predominantly and the intense features in the fluorescence spectrum shown in Figs. 1 and 2 to arise from the $SO(B\ {}^3\Sigma^-\ (v' = 2) \rightarrow X\ {}^3\Sigma^-\ (v'' = n))$ progression. It should be noted that the observed bands show a small $(0.3\ nm \equiv 33\ cm^{-1})$ systematic shift from the positions expected from published data. This is due to the selective excitation of rotational levels with $J'' \approx 12 - 26$ as transitions from these levels overlap most favourably with the laser line. This effect has been noted previously [2, 7].

This conclusion is in agreement with the recent proposal made by Wilson *et al.* [7] who reported the same bands but with emphasis on the region 380 - 440 nm. In addition they reported an upper limit for the radiative lifetime of the emitting state which is consistent with that for the $B\ {}^3\Sigma$ state [14]. The longer radiative lifetime reported previously [6] was determined from the bands at shorter wavelengths (250 - 270 nm) and must either result from weaker emission from $SO\ A\ {}^3\Pi_i$ or possibly residual emission from $SO_2\ \tilde{B}\ {}^1B_1$. If the population of the $v'' = 0$ level of $SO\ X\ {}^3\Sigma^-$ were very much larger than that for the $v'' = 2$ level, this could compensate for the weaker transition moment for the A–X system relative to the B–X system and result in significant pumping of the $A\ {}^3\Pi_2\ (v' = 5)$ and $A\ {}^3\Pi_0\ (v' = 6)$ levels. Fluorescence from these levels is expected to be most intense in the region 250 - 270 nm and the intensity in this region is in fact slightly higher than that expected from the Franck–Condon factors for the B–X system alone. Optical pumping of the $B\ {}^3\Sigma^-$ state from the $X\ {}^3\Sigma^-\ (v'' = 0)$ level is not possible at 248 nm. The time resolution available in the first reported experiments [6] would not have allowed the observation of fast emission from $SO\ B\ {}^3\Sigma^-$.

Finally, we note that the structure observed at 290 - 310 nm (Fig. 1) appears only at high pressures of SO_2 $(P_{SO_2} \geqslant 200\ N\ m^{-2})$ and is due to self-absorption [10] by SO_2.

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