



VUV photoabsorption spectroscopy of sulphur dioxide in the 1400–1600 Å region: Vibronic analysis of the $\tilde{E}-\tilde{X}$ system

Param Jeet Singh, Aparna Shastri*, R. D'Souza, S.V.N. Bhaskara Rao, B.N. Jagatap

Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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ABSTRACT

Gas phase photoabsorption studies of sulphur dioxide are carried out in the vacuum ultraviolet region using synchrotron radiation. Vibronic Analysis of the $\tilde{E}-\tilde{X}$ system lying in the region 1400–1600 Å is reported for the first time. A larger number of spectral features are resolved compared to earlier reports. While most of the observed bands can be arranged into four series with successive band spacing of 500–620 cm^{-1} in agreement with previous work, we observe two additional series with average separation of ~ 1750 and $\sim 1000 \text{ cm}^{-1}$. Results of the *ab initio* calculations suggest that at least three dominant excitations are involved in the $\tilde{E}-\tilde{X}$ system viz. $\tilde{X}^1A_1 \rightarrow \tilde{3}^1A_1$, $\tilde{X}^1A_1 \rightarrow \tilde{2}^1A_2$ and $\tilde{X}^1A_1 \rightarrow \tilde{2}^1B_1$. The observed vibrational features are found to be mainly due to excitation of the combination modes $(\nu_1 + \nu_2)$ and $(\nu_2 + \nu_3)$ with some contributions from ν_1 and ν_3 . Details of the experiment and analysis are discussed in this paper.

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1. Introduction

Sulphur dioxide (SO_2) is a common atmospheric pollutant and is also found in planetary atmospheres and interstellar medium; the sulphur cycle playing an important role in the atmosphere of Venus and Io [1–3]. On the earth, the major source of SO_2 in the stratosphere is from volcanic emissions whereas tropospheric SO_2 is known to arise mainly from fossil fuel combustion. Quantitative measurements of SO_2 from volcanic eruptions have been recently performed by satellite based detection in the UV/visible region [4]. SO_2 is a precursor of sulphates, which form major components of tropospheric and stratospheric aerosols and acid rain [5]. These reactions are initiated by the oxidation of SO_2 either by chemical reactions or photolysis. Due to its impact on the environment, photochemistry of SO_2 has been studied quite extensively [5,6 and references therein]. An understanding of the electronically excited states of SO_2 is of paramount

importance in gaining an insight into its complex photochemistry.

The electronic absorption spectrum of SO_2 extends from visible to VUV-soft X-ray regions and exhibits rich and complex structure. Photoabsorption studies of SO_2 in the UV-visible and VUV regions have concentrated mainly on absorption cross section measurements due to the importance of this data in astrophysics and environmental sciences [3,7–14]. The first electronic absorption bands lie in the visible region above 3500 Å ($< 3.5 \text{ eV}$) and involve excited triplet states [15,16]. The next region viz. 2500–3500 Å (3.5–5.0 eV) shows an intense absorption system due to a forbidden transition, which is made allowed via the Herzberg-Teller effect [16]. Interestingly, the geometries of the upper electronic states in the first two excited states differ considerably from the ground state geometry and also from each other. The $\tilde{X}^1A_1 \rightarrow \tilde{C}^1B_2$ system of SO_2 lying in the 1700–2300 Å region has been the subject of numerous investigations [17–21]. Analysis of the vibronic structure in this region has led to the conclusion that the geometry of the excited state is not only considerably different, but also has unequal SO bond lengths resulting in a modification of

* Corresponding author. Tel.: +91 22 25590343; fax: +91 22 25502652.
E-mail address: ashastri@barc.gov.in (A. Shastri).

the point group from C_{2v} in the ground state to C_s in the excited state [20,21]. In the deeper VUV region, i.e. $< 1700 \text{ \AA}$ ($> 7.3 \text{ eV}$), gas phase photoabsorption studies of SO_2 are few and sparse [12,22,23]. The VUV absorption spectrum of SO_2 in the wavelength region $1380\text{--}1600 \text{ \AA}$ ($7.7\text{--}9.0 \text{ eV}$) corresponds to the system classically designated as $\tilde{E}-\tilde{X}$ [15,16,22]. Early VUV studies have reported the presence of three diffuse bands in the region $1400\text{--}1600 \text{ \AA}$ [15], a picture revised later with the advent of better VUV sources and optical equipment. Holtom et al. [24] have carried out VUV photoabsorption studies on SO_2 ice with a view to understand the behavior of SO_2 ice in the interstellar medium. They have concluded that while the gas phase spectrum indicates the presence of a single excited state, electron impact studies [25–28] suggest that there may be two electronic states in this region, one of which is a triplet. The atmospheric

importance of the molecule has prompted several studies probing photodissociation dynamics proceeding through excitation to the $\tilde{E}$ state [5,6 and references there in]. Two-photon pump–probe experiments in the region of the $\tilde{E}$ state show that photodissociation in this region proceeds via cleavage of an S–O bond to form sulphur monoxide in an excited state [6]. To the best of our knowledge detailed vibronic analysis of the $\tilde{E}-\tilde{X}$ system has not been reported so far. There exist a few earlier reports which have attempted to analyze this system, but with limited success [16,22]. For example, theoretical calculations by Palmer et al. [16] predict several singlet and triplet valence electronic states with high oscillator strength lying between 7.6 and 9.2 eV . However no definitive conclusions regarding the excited electronic and vibrational states involved in the transitions have been drawn.

The absence of detailed studies leading to concrete spectroscopic assignments and understanding of the symmetries of the excited states in the $\tilde{E}-\tilde{X}$ system has stimulated the present study. In this paper we investigate experimentally and theoretically the photoabsorption spectrum of SO_2 in the $7.6\text{--}9.2 \text{ eV}$ region. Comparison of the experimental data and theoretical calculations is used to suggest the dominant vibronic excitations in this region.

2. Experimental

Photoabsorption studies of sulphur dioxide are carried out at a resolution of $\sim 0.3 \text{ \AA}$ using the High Resolution VUV beamline at Indus-1, RRCAT, Indore. Details of this beamline and experimental setup may be found in our earlier publication [29]. The beamline uses a 6.65 m off-plane Eagle spectrometer for wavelength dispersion. The central wavelength of interest is chosen by an appropriate rotation and translation of the grating, and the spectrum is scanned by moving an exit slit-cum-PMT assembly along the Rowland circle. The measurements were made with a 1200 g/mm grating mounted in

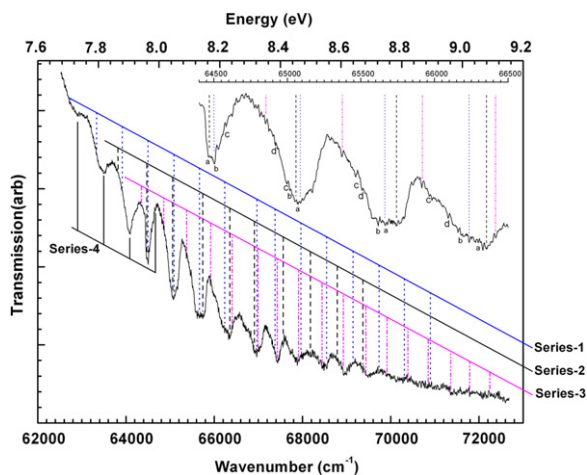


Fig. 1. VUV photoabsorption spectrum of the $\tilde{E}-\tilde{X}$ system recorded using the HRVUV beamline at Indus-1. The inset shows an expanded view of the spectral region $64,400\text{--}66,500 \text{ cm}^{-1}$.

Table 1

List of observed bands in the photoabsorption spectrum of the $\tilde{E}-\tilde{X}$ system of SO_2 .

S.No.	Series-1	Series-2	Series-3	Series-4	Series-5	Series-6
1	62,740	63,820	64,345	62,903	62,740	63,335
2	63,335	64,470	64,855	63,493	64,500	64,345
3	63,915	65,108	65,375	64,088	66,236	65,375
4	64,500	65,740	65,920	64,668	67,961	66,418
5	65,088	66,353	66,418		69,729	67,428
6	65,663	66,965	66,930		71492	68,438
7	66,236	67,560	67,428			69,440
8	66,810	68,160	67,920			70,390
9	67,381	68,780	68,438			71,360
10	67,961	69,370	68,938			72,356
11	68,549		69,440			
12	69,139		69,910			
13	69,729		70,390			
14	70,307		70,858			
15	70,885		71,360			
16			71,795			
17			72,255			
Average separation	582	617	495	588	1750	1002

All values are in cm^{-1} . Uncertainties in measurements are within $\pm 12 \text{ cm}^{-1}$.

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