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Interaction of 4 μm laser beam with absorption lines of sulphur dioxide

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Interaction of a free electron laser beam of wavelength 4 μm with rotational lines of sulphur dioxide has been studied. Values of transmittance, averaged over intervals of 0.1 cm^{-1}, are obtained for absorber thickness 0.01, 0.1 and 1 atm-cm, using the quasi-random model of molecular band absorption. From these values, intensities of the high resolution absorption lines of SO_2 are simulated in the frequency interval 2499.0115 – 2499.9910 cm^{-1}.

Keywords: Sulphur dioxide lines, Quasi-random model, Free electron laser, Transmittance

1 Introduction

Sulphur dioxide is an interesting molecule for basic science, in particular in comparison to the isoelectronic O_3 molecule. Moreover, it is an important astrophysical and atmospheric molecule. SO_2 enters the atmosphere as a result of both natural phenomena and anthropogenic activities, e.g. combustion of fossil fuels, oxidation of organic material in soils, volcanic eruptions and biomass burning. Coal burning is the single largest man-made source of sulphur dioxide, accounting for about 50% of annual global emissions, with oil burning accounting for a further 25-30%[1]. Lasers are increasingly used in pollution control studies and monitoring the environment. Hence precise knowledge of the spectra of sulphur dioxide is imperative for accurate measurements involving the passage of a laser beam through this gaseous medium.

In this study, a free electron laser, tuned to 4.0 μm, is considered. The frequency interval, 2499.0115 – 2499.9910 cm^{-1}, in which the propagation of this free electron laser beam is considered lies in the combination vibration – rotation $\nu_1+\nu_3$ band of SO_2. The combination vibration – rotation $\nu_1+\nu_3$ band of SO_2 was recorded under Doppler limited and atmospheric conditions using a cw difference-frequency spectrometer with 3×10^{-4} cm^{-1} instrumental resolution by mixing of an argon-ion laser with a tunable dye laser in the nonlinear optical crystal $LiNbO_3$[2]. Anhydrous grade (99.98% purity) SO_2 was used in that experiment. Three cells were used with CaF_2 windows slightly wedged to prevent channeling. The 1 m long reference cell was filled with 2 torr of N_2O, the 1.015 m long Doppler-limited cell was filled with 1.01 torr of SO_2 and the 1m long atmospheric cell was filled with 7.5 torr of air. The spectra were recorded at room temperature, 294 K.

The quasi-random model, which is one of the elementary models of molecular band absorption, can be used to simulate the intensities of these lines. Infrared transmittances, based on the quasi-random model, have been calculated for H_2O and CO_2 and the results fitted with experimental measurements[3,4]. Using this model, simulations of intensities of absorption lines have been done for p-benzoquinone-H_4 vapour[5] in the region 17800 - 24900 cm^{-1}, for water vapour[6] around 1.15 μm, and for nitrogen[7] around 575 nm. Potential use of this model in developing rapid models for accurately calculating atmospheric transmittances has been indicated[8]. Recently, simulating the intensities of high-resolution lines of nitrogen around 570 nm, applicability of this model in optics of the atmosphere, especially of the upper atmosphere, has been shown[9].

2 Theory

2.1Quasi-random Model

A detailed description of the quasi-random model can be found elsewhere[10]. Distinguishing features of this model are as follows. The quasi-random model characterises the wing effects accurately, i.e. it takes into account the absorption of spectral lines in as many neighbouring intervals as necessary. Each interval Ω, over which the average transmittance is required, is further divided into smaller intervals δ. Each line may be said to be localized within an error defined by the interval size δ. These elementary intervals are chosen small enough to ensure an accurate description of the important band characteristics, yet large enough to simplify the calculations. All the lines falling within a given order of magnitude are subsequently averaged, and each line in each intensity sector is then associated with the appropriate average value. Since the top five intensity sectors in each frequency interval are found to be sufficient to describe the absorptive properties associated with the lines therein, the transmittance at a frequency ν as affected by the n_p lines in the frequency interval δ_p is given by[11].

$$\mathrm{T}(\nu)=\prod_{i=1}^{5}\left\{\left(\frac{1}{\delta}\right)\int_{\delta_p}\exp\left[-S_i u b(\nu,\nu_i)\right]d\nu_i\right\}^{n_i} \quad \ldots (1)$$

where n_i represents the number of lines within the intensity range i, which itself is characterised by an average intensity S_i, u is the absorber thickness in atm-cm (atmosphere centimetre), and $b(\nu,\ \nu_i)$ is the Lorentz shape factor defined by

$$b(\nu,\nu_{\mathrm{i}})=\frac{\alpha/\pi}{(\nu-\nu_i)^2+\alpha^2} \quad \ldots (2)$$

(α is the half-width, i.e. half the frequency difference between the half-maximum points, ν_i refers to the centre of the line).

Table 1— SO_2 lines affecting the propagation of the 4 μm laser beam

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
2499.888	.11	2499.408	.17
24988989	.46	2499.417	.09
2498.9574	.56	2499.437	.07
2498.966	.19	2499.4454	.43
2498.986	.14	2499.4835	.50
2499.0115	.62	2499. 488	.21
2499.0241	.45	2499.5149	.82
2499.0593	.73	2499.5421	.82
2499.0875	.35	2499.552	.09
2499.1021	.83	2499.5687	.25
2499.112	.20	2499.6021	.31
2499.1392	1	2499.612	.15
2499.1461	.44	2499.627	.09
2499.1749	.21	2499.6366	.37
2499.200	.47	2499.6620	.45
2499.221	.12	2499.6840	.65
2499.2433	.27	2499.689	.19
2499.248	.56	2499.7307	.21
2499.284	.11	2499.761	.17
2499.2914	.66	2499.7749	.27
2499.3001	.29	2499.7842	.42
2499.3282	.73	2499.7905	.13
2499.347	.15	2499.824	.08
2499.3547	.35	2499.8982	.20
2499.3607	.91	2499.914	.09
2499.379	.11	2499.924	.11
2499.396	.19	2499.961	.09
2499.4024	.39	2499.991	.08

2.2 Calculation of absorptance

The calculation of the transmittance requires knowledge of the frequency and intensity of each and every spectral line which contributes significantly to the absorption in the frequency range of interest. The entire spectrum in the range 2499.0115 – 2499.9910 cm^{-1} is divided into frequency intervals 0.1 cm^{-1} (Ω) wide. Each interval is divided into smaller intervals 0.025 cm^{-1} (δ). The maximum value is normalized to unity, and other values of intensity are taken relative to this one. The lines considered are given in Table 1 along with the assigned intensities. The half width of the lines is taken as 0.015 cm^{-1}. Using Simpson's rule of numerical integration, Eq. (1) is evaluated with the help of a computer program for three different masses per unit area (u): 0.01, 0.1 and 1 atm-cm. First, the transmittance values are calculated at the centres of 0.1 cm^{-1} intervals. Transmittances by the wings of lines at the left and right adjacent intervals are also included. The transmittance at the centre of an interval is finally obtained as[4]:

$$T = T_{\mathrm{j}}\prod_{\mathrm{i}\neq\mathrm{j}}T_i \quad \ldots (3)$$

The transmittance values are obtained for another set of frequency intervals whose centres are shifted by half the interval size (0.05 cm^{-1}) from the original positions of the centres of the intervals. This is done in order to minimise the error associated with the occurrence of lines at frequencies near the edges of a given interval. The results for the shifted and un-shifted intervals are averaged, and thus we obtain the average transmittance over a 0.1 cm^{-1} interval.

Table 2 — Absorption of a 4 μm laser beam for three different amounts of SO_2

Frequency (cm^{-1})	Absorption (%) for path length 0.01 atm-cm	1 atm-cm	1 atm-cm
2499.0615	45.35	46.21	54.04
2499.1615	51.34	53.74	67.7
2499.2615	56.60	69.19	90.66
2499.3615	61.90	90.43	100
2499.4615	62.40	91.68	100
2499.5615	60.44	84.06	99.53
2499.6615	55.09	61.18	82.17
2499.7615	50.09	50.94	58.64
2499.8615	43.94	44.28	47.53
2499.9615	29.86	29.96	30.99

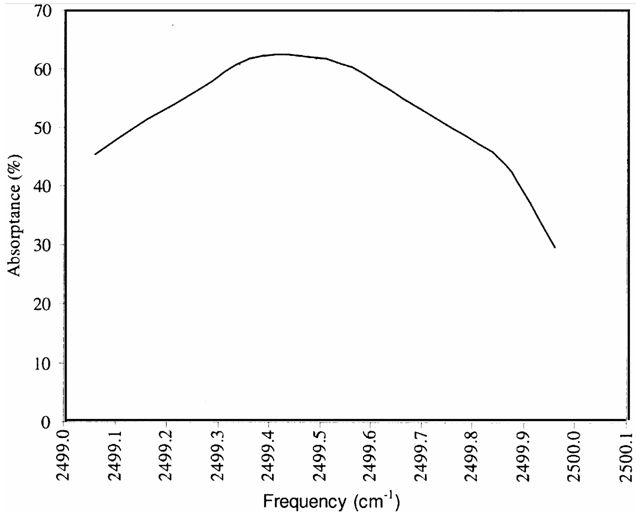

Fig. 1 — Absorptance of a 4 μm free electron laser beam for a 0.01 atm-cm path length of SO_2

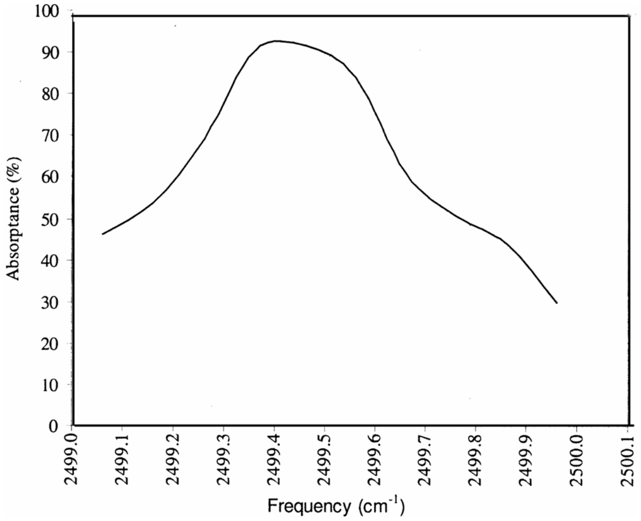

Fig. 2 — Absorptance of a 4 μm free electron laser beam for a 0.1 atm-cm path length of SO_2

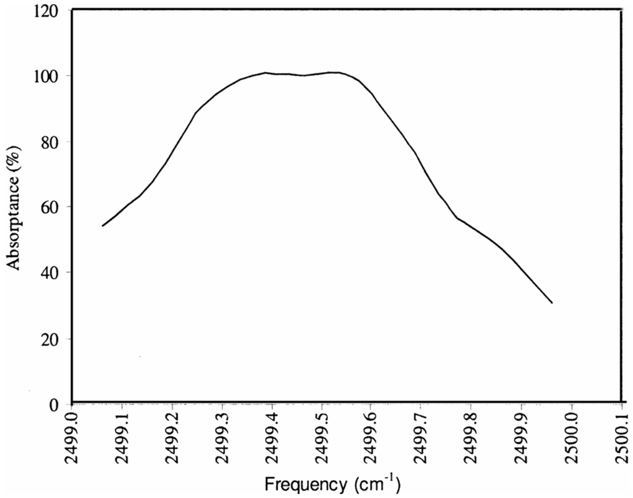

Fig. 3 — Absorptance of a 4 μm free electron laser beam for a 1.0 atm-cm path length of SO_2

3 Results and Discussion

Influences of 56 lines, 51 within and 5 outside the interval, are worked out for 0.01, 0.1 and 1 atm-cm thickness of sulphur dioxide. The computational results for the propagation of a 4 μm laser beam through these three path lengths of the absorber are presented in Table 2, and shown in Figs 1-3, respectively, which agree well with the experimental data taken for this work. This verifies that the quasi-random model for simulating the intensity distribution by grouping the lines in a given frequency interval works reasonably well. As the amount of the absorber becomes larger, more lines will have effects on the absorptance values, which is the reason for the appearance of the shoulder around 2499.56 cm^{-1} as well as flattening of the one around 2499.86 cm^{-1} in Fig. 3. The (relatively) strong absorption line at 2499.3607 cm^{-1} is responsible for the peak around this region in Fig. 2, which is not so marked for the smaller as well as the larger amounts of the absorber in Figs 1 and 3, respectively. At these frequencies, for the smaller amount the difference in the absorption values is small while for the larger amount more lines affecting absorption values diminish the peak. In this work, the broadening of the lines is assumed to be homogeneous, as the rotational lines are observed to be sufficiently fine. Therefore, there is a scope to generalize the model for inhomogeneous broadening as well. The application prospect of this model in atmospheric optics is quite bright. The $\nu_1 + \nu_3$ band of SO_2 is strategically located in the 4 μm atmospheric window which is convenient for monitoring SO_2 in the air or observing extraterrestrial SO_2 through the atmosphere.

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