An ASAP treatment of vibrationally excited S₂O: The ν_3 mode and the $\nu_3 + \nu_2 - \nu_2$ hot band

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Abstract

The fundamental S–S stretching mode ν_3 of disulfur monoxide, S₂O, located at 679 cm^{−1}, has been investigated using Fourier-transform far-infrared spectroscopy at the SOLEIL synchrotron facility. A spectroscopic analysis has been performed using an *Automated Spectral Assignment Procedure* (ASAP) which permits accurate determination of more than 2000 energy levels from ν_3 . In addition, the $\nu_3 + \nu_2 - \nu_2$ hot band was observed for the first time and some 500 corresponding energy levels were assigned. The high-resolution synchrotron study was complemented with pure rotational spectra of S₂O in the $(v_1, v_2, v_3) = (0, 0, 1)$ vibrational state observed in the frequency range

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from 250 to 280 GHz using a long-path absorption cell. From these combined measurements, extensive molecular parameter sets have been determined and precise band centers have been derived for both vibrational bands.

Keywords: Fourier-transform spectroscopy, far-infrared, synchrotron radiation, millimeter-wave spectroscopy, disulfur monoxide, S₂O, radio-frequency discharge

1 In the course of a recent high resolution infrared study of the S₂O bending
2 vibrational mode ν_2 performed at the SOLEIL synchrotron facility [1], the
3 fundamental S–S stretching mode ν_3 – first studied by Lindenmayer et al.
4 [2] employing diode laser spectroscopy in selected wavenumber regions – was
5 observed in its entirety (Figure 1). The current status of high-resolution
6 spectroscopy of S₂O has been highlighted in Ref. [1] and will not be repeated
7 here. In this research note, the analysis of the ν_3 band and the associated
8 $\nu_3 + \nu_2 - \nu_2$ hot band – which was observed for the first time at high spectral
9 resolution – are described briefly.

10 The S–S stretching mode ν_3 of S₂O was observed on the AILES beamline
11 [3, 4] at SOLEIL in the range from 645 to 700 cm^{−1}. The ν_3 spectrum shown
12 in Figure 1 consists of a co-average of 100 individual scans and about 6 h of
13 integration time. The experimental conditions were similar to the ones used
14 to detect the ν_2 mode [1] ($R = 0.001$ cm^{−1}, radio frequency (RF) discharge
15 power of 500 W, absorption path length 36 m) except that no elemental sul-
16 fur was added to the cell during the RF discharge of SO₂. Wavenumber
17 calibration was performed using H₂O and D₂O [5, 6]. An *Automated Spec-*
18 *tral Assignment Procedure* (ASAP) introduced in Ref. [1] was employed for

19 spectroscopic analysis. For the ν_3 fundamental, following the terminology
 20 in Ref. [1], the ground vibrational state $(v_1, v_2, v_3) = (0, 0, 0)$ served as the
 21 *reference state* whereas the $(0, 0, 1)$ state was the *target state*. Since for the
 22 latter rotational and quartic centrifugal distortion constants were already
 23 known from previous diode laser and Fourier transform microwave work (see
 24 Table 1 and Refs. [2, 7]), the ASAP worked smoothly despite the fact that
 25 ν_3 is pure *a*-type band and, as a consequence, fewer spectra are available
 26 for the cross-correlation (multiplication) procedure (by comparison, ν_2 is an
 27 *a*-/b-type hybrid band, see Ref. [1] for additional details). In total, some
 28 2240 energy levels of ν_3 were derived in a straightforward fashion (covering
 29 $J \leq 84$, $K_a \leq 20$).

30 Closer inspection of spectrum 2 in Fig. 1 reveals the presence of a sec-
 31 ond vibrational band with a *Q*-branch band head slightly shifted to the red
 32 of the ν_3 *Q*-branch by some 2.5 cm^{-1} . On the assumption that this band
 33 is the hot band $\nu_2 + \nu_3 - \nu_2$, i.e., originating from the energetically lowest-
 34 lying bending mode ν_2 , initial predictions were based on the recent data for
 35 the ν_2 mode [1] to constrain the *reference state* rotational level energies for
 36 the ASAP. At high spectral resolution, the putative *target state* $(0, 1, 1)$ has
 37 been characterized previously by Fourier transform microwave spectroscopy,
 38 in which seven lines up to 30 GHz [7] and relatively low quantum numbers
 39 ($J \leq 3$, $K_a \leq 1$) were observed. From this data set, three rotational con-
 40 stants and one quartic centrifugal distortion (D_{JK}) constant were determined
 41 (Table 1). To further improve the initial description of the *target state*, the
 42 remaining four quartic distortion constants were estimated by correcting the
 43 corresponding constants of the $(0, 0, 1)$ state for the differences between those

44 of the $(0, 1, 0)$ and $(0, 0, 0)$ states from Ref. [1]. Higher order terms were fixed
 45 at values of the $(0, 0, 1)$ state (Table 1). The vibrational wavenumber of the
 46 band center was initially estimated from the Q -branch band head in Figure
 47 1. Using this approach, the ASAP yields readily identifiable vertical series in
 48 the cross correlation plots for different values of K_a up to 7 that are shifted
 49 only by a small amount ($5 \times 10^{-3} \text{ cm}^{-1}$) from the prediction. Within one it-
 50 eration of ASAP refinement, 485 energy levels up to $J \leq 64$ and $K_a \leq 11$
 51 were determined.

52 Complementary submillimeter-wave investigations of S_2O in the $(0, 0, 1)$
 53 state were also performed in Cologne. The experimental conditions in this
 54 study were the same as those used during the corresponding investigation of
 55 the $(0, 1, 0)$ and $(0, 2, 0)$ states [1], i.e. the RF discharge was struck through
 56 SO_2 alone and spectra were recorded using a millimeter-wave spectrometer
 57 described in detail previously [8]. In total, 72 lines were observed between
 58 250 and 280 GHz, covering $J \leq 29$ and $K_a \leq 19$.

59 The new infrared and millimeter wave data for both bands were included
 60 in the semi-global dataset² from Ref. [1] and the least-squares analysis
 61 was performed using Pickett's SPFIT/SPCAT-suite of programs [9] and a
 62 Watson-type Hamiltonian in the A -reduction. In the fit, uncertainties of
 63 0.0001 and 0.0002 cm^{-1} were used for the ASAP energy levels of the $(0, 0, 1)$
 64 and $(0, 1, 1)$ states, respectively, and 10 kHz for the millimeter wave transition
 65 frequencies. The complete line list and the fit file are given as Supplemen-

²The new semi-global fit presented here considers all high resolution pure rotational and rotation-vibration data from the $(0, 0, 0)$, $(1, 0, 0)$, $(0, 1, 0)$, $(0, 2, 0)$, $(0, 0, 1)$, and $(0, 1, 1)$ states.

66 tary Electronic Material. As indicated from the best-fit constants in Table
 67 1, the new parameter sets for both the $(0, 0, 1)$ and $(0, 1, 1)$ states have been
 68 greatly extended compared to earlier studies. As an example, for the $(0, 0, 1)$
 69 mode, the full set of sextic and even two octic constants have now been
 70 determined as have all five quartic and two sextic distortion constants for
 71 the $(0, 1, 1)$ combination mode. In addition, vibrational wavenumbers were
 72 determined to high precision for both bands, $\tilde{\nu}_{(0,0,1)} = 679.1364116(36) \text{ cm}^{-1}$
 73 and $\tilde{\nu}_{(0,1,1)} = 1056.936446(21) \text{ cm}^{-1}$. It should be noted however, that in the
 74 present spectral region calibration might suffer from the somewhat limited
 75 accuracy of the water frequency standard ($\approx 10^{-3} \text{ cm}^{-1}$)[5, 6].

76 In close-up views of the SOLEIL spectrum around 677.5 and 669.7 cm^{-1}
 77 (spectra 2 and 3 in Figure 1) the experimental data are compared against
 78 simulations of both the ν_3 fundamental and the $\nu_3 + \nu_2 - \nu_2$ hot band based on
 79 the best-fit parameters in Table 1. For both bands, the agreement between
 80 the experiment and simulation is extremely good.

81 Since vibrational modes of S_2O are readily excited in electrical and RF
 82 discharges (including overtones and combination modes, see, e.g., Refs. [1, 7])
 83 additional high-resolution spectroscopy of this fundamental sulfur-rich oxide
 84 should be possible in the future, work which promises to further improve
 85 knowledge of its rotational and vibrational energy pattern higher up in the
 86 potential energy well. Inclusion of the most recent high resolution spectro-
 87 scopic data into a new global model of S_2O (cf. Ref. [7]) as well as com-
 88plementary millimeter-wave measurements (such as a study of vibrational
 89 satellites of the $(1, 0, 0)$ state) are two such avenues we are currently pursu-
 90 ing.

Table 1: Molecular Parameters of S₂O in the (0,0,1) and (0,1,1) states^a.

Parameter	(0, 0, 1)		(0, 1, 1)	
	Ref. [2]	this work	Ref. [7]	this work
A_v	41915.368(49)	41915.51769(80)	42480.4(68)	42480.497(44)
B_v	5036.1446(74)	5036.16425(18)	5036.91332(73)	5036.91810(48)
C_v	4486.8797(70)	4486.89604(21)	4480.56649(73)	4480.56215(47)
$\Delta_{Jv} \times 10^3$	1.8835(44)	1.89320(11)	...	1.90242(68)
$\Delta_{JKv} \times 10^3$	-32.090(44)	-32.1260(17)	-33.34(58)	-33.193(59)
Δ_{Kv}	1.20937(69)	1.213303(33)	...	1.31011(45)
$\delta_{Jv} \times 10^3$	0.34341(92)	0.344670(62)	...	0.34857(25)
$\delta_{Kv} \times 10^3$	12.26(20)	12.426(24)	...	14.382(83)
$\Phi_{Jv} \times 10^9$	...	1.049(20)	...	1.04(17)
$\Phi_{JKv} \times 10^9$	...	51.1(62)	...	^b
$\Phi_{KJv} \times 10^6$	...	-4.971(25)	...	-4.78(66)
$\Phi_{Kv} \times 10^3$	...	0.12591(19)	...	^b
$\phi_{Jv} \times 10^9$	...	0.515(11)	...	^b
$\phi_{JKv} \times 10^9$	...	17.5(48)	...	^b
$\phi_{Kv} \times 10^6$	...	5.86(58)	...	^b
$L_{KKJv} \times 10^9$	...	0.673(24)	...	^b
$L_{Kv} \times 10^9$	...	-18.25(31)	...	^b
$\tilde{\nu} / \text{cm}^{-1}$	679.136537(92)	679.1364116(36)	1056.1(50) ^c	1056.936446(21)

Note. Units are MHz, unless otherwise noted. The 1σ uncertainties (in parentheses) are in units of the last significant digit. ^a Simultaneous fit to the rotational and rotation-vibration data of the (0,0,0), (1,0,0), (0,1,0), (0,2,0), (0,0,1) and (0,1,1) states. ^b Kept fixed at corresponding value of (0,0,1) state.

^c Ref. [10]

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101 Appendix A. Supplementary material

102 Supplementary data associated with this article can be found, in the
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Figure 1: The ν_3 fundamental band of S_2O centered at 679 cm^{-1} , as observed at SOLEIL (top spectrum 1). The total observation time was 6 h. Close inspection of spectrum 2 shows the Q -branch band head of the $\nu_3 + \nu_2 - \nu_2$ hot band in addition to that of the ν_3 fundamental. The line multiplet in spectrum 3 is dominated by strong $^qP_{28}$ transitions of the ν_3 fundamental but lines of the hot band are also clearly present there.

*Graphical Abstract

ν_3
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