Journal of Quantitative Spectroscopy & Radiative Transfer 240 (2020) 106686

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Notes

Line list for the $a^1\Delta$-$X^3\Sigma^-$ transition of SO: Assignment of the 1.69 micron feature on Io

Peter F. Bernath*, Dror M. Bittner[1]

Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States

ARTICLE INFO

Article history:
Received 9 August 2019
Revised 4 October 2019
Accepted 4 October 2019
Available online 7 October 2019

ABSTRACT

In order to simulate the observations of the $a^1\Delta$-$X^3\Sigma^-$ electronic transition of SO in thermal emission from Io, a moon of Jupiter, a line list for the 0–0 and 1–1 bands is calculated. A feature at 1.69 μm in the astronomical spectrum is assigned as the high-J $^rR_{12}$ band head using the 0–0 line list.

1. Introduction

The SO molecule is isovalent with O_2 and has an $X^3\Sigma^-$ ground state with low-lying metastable $a^1\Delta$ and $b^1\Sigma^+$ states. SO has been observed via pure rotational transitions in many interstellar clouds and is relatively abundant in star-forming regions such as the Orion nebula [1]. SO has been detected on Jupiter's moon Io by microwave transitions [2], by the $B^3\Sigma^-$-$X^3\Sigma^-$ ultraviolet transition [3] and the near infrared emission of the forbidden $a^1\Delta$-$X^3\Sigma^-$ transition near 1.7 μm [4].

SO spectra have been measured in the laboratory from the microwave to the ultraviolet spectral regions. Although nominally forbidden, the $b^1\Sigma^+$-$X^3\Sigma^-$and $a^1\Delta$-$X^3\Sigma^-$ transitions have been recorded in the near infrared region at high resolution near 955 nm and 1.7 μm, respectively [5,6]. The corresponding transitions for the symmetric O_2 molecule are mainly magnetic dipole in character but they are primarily electric dipole for SO due to the absence of inversion symmetry [7]. In O_2 the Einstein A values for the $b^1\Sigma^+$-$X^3\Sigma^-$and $a^1\Delta$-$X^3\Sigma^-$ transitions are about 0.083 s^{-1} and 2.5×10^{-4} s^{-1}, respectively [7]. The $b^1\Sigma^+$, $a^1\Delta$ and $X^3\Sigma^-$ states in SO are not pure Hund's case (a) states because of spin–orbit coupling and this contamination makes the transitions allowed. For example, the Breit–Pauli spin–orbit operator allows the $a^1\Delta$ state to mix with $^3\Pi$ states and the $X^3\Sigma^-$ state to mix with $^1\Sigma^+$, $^3\Pi$ and $^1\Pi$ states [7].

To assign the carrier of the 1.77 μm feature on Io and estimate a temperature [4], a line list was created by refitting the lines measured by Setzer et al. [6] and calculating the relative rotational line strengths with Hönl-London factors for a magnetic dipole transition [8]. The simulated spectra successfully matched the observations taken with a resolving power of about 2000 with a temperature of about 1000 K except for an unassigned feature at 1.69 μm. We present here a new line list for the 0–0 and 1–1 bands of the $a^1\Delta$-$X^3\Sigma^-$ transition and can now assign the 1.69 μm feature.

2. Method

The lines of 0–0 bands of the $a^1\Delta$-$X^3\Sigma^-$ transition were refitted using a standard $\boldsymbol{N}^2$ Hamiltonian [9] and the molecular constants were input to Western's PGOPHER [10] program (see supplementary data for the values). The radiative lifetime of the $a^1\Delta$ state was estimated to be 0.45 s [7] corresponding to an Einstein A value of 2.22 s^{-1}, which converts to a transition dipole moment of 0.0059 D [11]. This transition moment was used as the band strength in PGOPHER. The maximum J was set to 150 and the line list was exported from PGOPHER (see supplementary information) with line strengths in the form of Einstein $A_{J'\rightarrow J''}$ values. The wavenumber error in the line positions is about 0.001 cm^{-1} up to about $J=35$; line positions at high J are therefore extrapolations with errors at $J=80$ of about 0.04 cm^{-1} based on propagation of errors from the rotational constants [6]. The accuracy of the line strengths is hard to assess because Klotz et al. [7] report no error estimate for the calculated lifetime but could easily be a factor of 2 (or more). The reported Einstein $A_{J'\rightarrow J''}$ values can be converted to oscillator strengths, transition dipole moments or HITRAN units with the equations in Bernath's textbook [11].

For the 1–1 band the spectroscopic data were obtained from an absorption spectrum of the 1–0 fundamental bands of both the ground $X^3\Sigma^-$ state and the metastable $a^1\Delta$ state [12]. The spec-

* Corresponding author.
E-mail address: pbernath@odu.edu (P.F. Bernath).
[1] Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel

https://doi.org/10.1016/j.jqsrt.2019.106686
0022-4073/

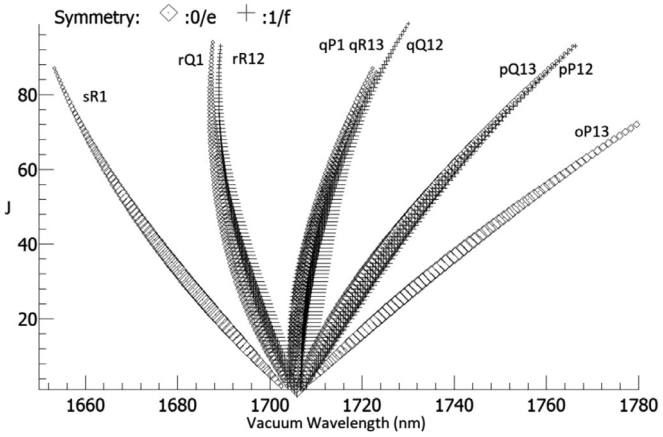

Fig. 1. Fortrat diagram of the 0–0 band of the $a^1\Delta$-$X^3\Sigma^-$ transition.

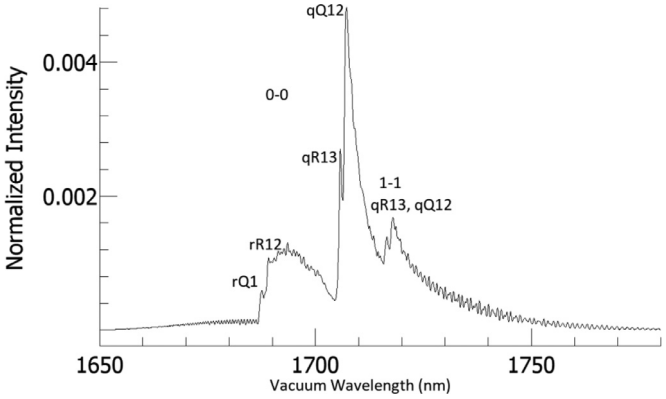

Fig. 2. Simulation of the $a^1\Delta$-$X^3\Sigma^-$ transition at low resolution (see text).

troscopic constants of Burkholder et al. [12] were used for $v=1$ of both states. The $a^1\Delta$ $v=1$ spectroscopic constants were transformed to make them compatible with the energy level expression used by PGOPHER. The transition dipole moment used was the same as for the 0–0 band, and the 1–1 line list with $J_{max} = 100$ is also provided as supplementary data. Errors in the line positions are about 0.001 cm^{-1} at low J and increase to about 0.005 cm^{-1} for the last observed J of 31.

3. Results and discussion

The usual electric dipole selection rules on J ($\Delta J = 0, \pm1$ and $+\leftrightarrow-$ for total parity) [11] result in 9 branches for a $^1\Delta$-$^3\Sigma^-$ transition: $^oP_{13}$, $^pP_{12}$, $^pQ_{13}$, $^qQ_{12}$, $^qR_{13}$, $^qP_1$, $^rR_{12}$, $^rQ_1$ and $^sR_1$ [6]. The lines are labeled using the traditional notation, $^{\Delta N}\Delta J_{Fi'Fj''}(J'')$: the left superscript is ΔN (**N=J–S**) written in lower case with o, p, q, r and s corresponding to ΔN=−4, −2, 0, 2 and 4, respectively; ΔJ in upper case is P, Q and R for $\Delta J = -1$, 0 and 1, respectively; the right subscript is Fi′Fj″, in which Fi′ is 1 ($N=J$) for the upper $a^1\Delta$ state and Fj″ is 1, 2 or 3, for $J=N+1$, $J=N$ and $J=N-1$, respectively (energy level diagrams are available, for example in [11]); prime and double prime refer to upper and lower energy levels, respectively. The "form" of the branches (ΔN) is a convenient label because near the band origin o, p, q, r and s form branches are spaced by approximately −4B, −2B, 0B, +2B, +4B (Fig. 1) with the rotational constant B of about 0.71 cm^{-1}. This is illustrated in Fig. 1 with a Fortrat diagram drawn with wavelength on the x-axis.

The spectrum (Fig. 2) is simulated with a temperature of 1600 K and vibrational temperature of 1000 K with a Gaussian linewidth of 0.5 nm. The main feature is the strong $^qQ_{12}$ branch near the origin with the nearby $^qR_{13}$ band head which forms at $J'' = 6$ at 1705.573 nm (5863.132 cm^{-1}). The $^rR_{12}$ branch forms a head at about $J'' = 81$ at 1688.89 nm (5921.05 cm^{-1}) and the weaker $^rQ_1$ head at 1687.21 nm (5926.96 cm^{-1}) with $J'' = 82$. The last measured rotational level in the laboratory has $J'' = 36$ [6] so the wavelengths of these heads are extrapolated. Comparison of Fig. 2 with the spectrum of Io [4] clearly shows the strong $^qQ_{12}$ branch, a hint of the $^qR_{13}$ head, the $^rR_{12}$ head at 1.689 µm and a hint of the 1–1 band $^qQ_{12}$ branch at 1.713 µm. The comparison suggests that SO is not in thermodynamic equilibrium because the $^rR_{12}$ head is stronger than expected and the 1–1 $^qQ_{12}$ branch is weaker than expected. The lack of thermodynamic equilibrium is also suggested by observations of Io at higher spectral resolution [13].

4. Conclusions

Line lists have been calculated for the 0–0 and 1–1 bands of the $a^1\Delta$-$X^3\Sigma^-$ electronic transition of SO. These line lists have identified the 1.69 µm feature on Io as the 0–0 $^rR_{12}$ band head that appears with enhanced intensity because of a lack of thermodynamic equilibrium. The 1–1 band may also be present in the spectrum of Io. The new line lists can be used to determine the population distribution in the $a^1\Delta$ energy levels and perhaps an independent estimate of the $a^1\Delta$-state abundance from the Einstein A-values. Note that the stronger $b^1\Sigma^+$-$X^3\Sigma^-$ transition of SO ($A = 175$ s^{-1} [14], compared to an estimated value of 2 s^{-1} for the a-X transition) has not yet been detected on Io. The preparation of improved line lists is underway by simultaneous fitting all observed line positions and *ab initio* calculation of the a-X transition dipole moment.

Declaration of Competing Interest

None.

Acknowledgments

Funding was provided by the NASA Laboratory Astrophysics Program through grant 80NSSC18K0240 to PFB.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2019.106686.

References

[1] Esplugues GB, Tercero B, Cernicharo J, Goicoechea JR, Palau A, Marcelino N, et al. A line confusion-limited millimeter survey of Orion KL III. Sulfur oxide species. Astron Astrophys 2013;556:A143.
[2] Lellouch E, Strobel DF, Belton MJS, Summers ME, Paubert G, Moreno R. Detection of sulfur monoxide in Io's atmosphere. Astrophys J Lett 1996;459:L107–10.
[3] McGrath MA, Belton MJS, Spencer JR, Sartoretti P. Spatially resolved spectroscopy of Io's Pele Plume and SO_2 atmosphere. Icarus 2000;146:476–93.
[4] de Pater I, Roe H, Graham JR, Strobel DF, Bernath P. Detection of the forbidden SO $a^1\Delta$-$X^3\Sigma^-$ rovibronic transition on Io at 1.7 µm. Icarus 2002;156:296–301.
[5] Colin R. The $b^1\Sigma^+$-$X^3\Sigma^-$band system of SO. Can J Phys 1968;46:1539–46.
[6] Setzer KD, Fink EH, Ramsay DA. High-resolution Fourier transform study of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ and $a^1\Delta \rightarrow X^3\Sigma^-$ transitions of SO. J Mol Spectrosc 1999;198:163–74.
[7] Klotz R, Marian CM, Peyerimhoff SD, Hess BA, Buenker RJ. Calculation of spin–forbidden radiative transitions using correlated wavefunctions: lifetimes of $b^1\Sigma^+$, $a^1\Delta$ and $X^3\Sigma^-$ states in O_2, S_2, and SO. Chem Phys 1984;89:223–36.
[8] Bellary VP, Balasubramanian TK. On the rotational intensity distribution in the $a^1\Delta_g \rightarrow X^3\Sigma^-_g$ magnetic dipole transition of oxygen molecule. J Mol Spectrosc 1987;126:436–42.
[9] Brown J, Carrington A. Rotational spectroscopy of diatomic molecules. Cambridge, UK: Cambridge University Press; 2003.
[10] Western CM. PGOPHER: A program for simulating rotational, vibrational and electronic spectra. J Quant Spectrosc Radiat Transf 2017;186:221–42.

[11] Bernath PF. Spectra of atoms and molecules. 3rd Ed. NY: Oxford University Press; 2016.
[12] Burkholder JB, Lovejoy ER, Hammer PD, Howard CJ. High-Resolution infrared Fourier transform spectroscopy of SO in the $X^3\Sigma^-$ and $a^1\Delta$ electronic states. J Mol Spectrosc 1987;124:379–92.
[13] de Kleer K, de Pater I, Ádámkovics M. Emission from volcanic SO gas on Io at high spectral resolution. Icarus 2019;317:104–20.
[14] Wildt J, Fink EH, Winter R, Zabel F. Radiative lifetime and quenching of SO ($b^1\Sigma^+$,$v' = 0$). Chem Phys 1983;80:167–75.