

Quantum Mechanical Treatment of Normal Modes in Polyatomic Molecules

The wave function equation for an N-atom molecule is given by:

$$\frac{-\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \left[\frac{\partial^2 \Psi}{\partial x_i^2} + \frac{\partial^2 \Psi}{\partial y_i^2} + \frac{\partial^2 \Psi}{\partial z_i^2} \right] + V(x_1, y_1, \dots, z_N) \Psi = \sum_{i=1}^N \bar{E}_i(x_i, y_i, z_i) \Psi$$

Briefly,

$$\frac{-\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 \Psi + V \Psi = \bar{E} \Psi$$

3N coordinate (Cartesian) will yield (non-linear):

3 translations,

3 rotations, and

3N-6 vibrations (or normal coordinates).

$$T = \frac{1}{2} \sum_i \dot{Q}_i^2$$

$$V = \frac{1}{2} \sum_i \lambda_i Q_i^2$$

H = T + V (Classical Hamiltonian)
using mass weighted coordinates (Q)

λ_i is angular frequency related to force constant.

Q_i is normal mode coordinate (3N-6 or 3N-5)

Transition from classical mechanics to quantum mechanics:

$$Q_i \rightarrow \hat{Q}_i$$

$$P_i \rightarrow \hat{P}_i = -i\hbar \frac{\partial}{\partial Q_i}$$

mass-weighted

$$\downarrow \left(\dot{Q}_i = \frac{dQ_i}{dt} = P_i \right)$$

The QM Hamiltonian is then:

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i \lambda_i \hat{Q}_i^2 = \sum_i \hat{H}_i$$

i goes from 1 to $3N-6$ (or $3N-5$).

The Hamiltonian operator equation ($\sum_i \hat{H}_i$) is a sum of $3N-6$ independent H.O. Hamiltonian operators

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \dots + \hat{H}_{3N-6}$$

For each we have

$$\hat{H}_1 \psi_1(Q_1) = E_1 \psi_1(Q_1)$$

$$\hat{H}_2 \psi_2(Q_2) = E_2 \psi_2(Q_2)$$

$$\vdots$$

$$\hat{H}_{3N-6} \psi_{3N-6}(Q_{3N-6}) = E_{3N-6} \psi_{3N-6}(Q_{3N-6})$$

} $3N-6$ independent S.E.'s.

It is important to note that the Schrodinger equation is composed of a number of wavefunctions, ψ , equal to $3N-6$ (or $3N-5$) independent ones:

$$\Psi = \psi_1(Q_1) \psi_2(Q_2) \dots \psi_{3N-6}(Q_{3N-6})$$

with

$$\psi_i(Q_i) = N_{\nu_i} H_{\nu_i} \left(Q_i \sqrt{\frac{\lambda_i}{\hbar}} \right) \exp\left(-\frac{Q_i^2}{\hbar} \sqrt{\lambda_i}\right)$$

where Q is the normal mode coordinate.

Skip

In practice:

The Cartesian coordinate ($3N$)

(x_1, y_1, \dots, z_N)

\Downarrow transformed

Internal coordinate ($3N-6$)

$(R_1, r_1, \alpha_1, \dots)$

\Downarrow Group theory

Symmetry coordinates

$(S_1 = R_1 + R_2, \dots \text{etc.})$

\Downarrow calculation

Normal coordinates

$(Q_1, Q_2, \dots, Q_{3N-6})$

As each normal coordinate has its own wave function $\psi_i(Q_i)$, each can be represented by its own Schrödinger equation:

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi_i(Q_i)}{dQ_i^2} + \frac{1}{2} \lambda_i Q_i^2 \psi_i(Q_i) = E_i \psi_i(Q_i)$$

$i = 1, 2, \dots, 3N-6$

Each Q_i normal coordinate has its own energy.

$$E_i = \hbar \omega_i \left(\nu_i + \frac{1}{2} \right)$$

$$\therefore \omega_i = 2\pi \nu_i$$

$$E_i = \hbar \nu_i \left(\nu_i + \frac{1}{2} \right) \quad \nu_i = \frac{\omega_i}{2\pi}$$

$$E_i = \hbar \lambda_i^{1/2} \left(\nu_i + \frac{1}{2} \right) \quad \text{or } \omega_i = \lambda_i^{1/2}$$

The total energy (E_{vib}) is the sum of the $3N-6$ (or $3N-5$) energies:

$$E_{\text{vib}} = \hbar \omega_1 \left(\nu_1 + \frac{1}{2} \right) + \hbar \omega_2 \left(\nu_2 + \frac{1}{2} \right) + \dots + \hbar \omega_{3N-6} \left(\nu_{3N-6} + \frac{1}{2} \right)$$

$$= \sum_i \hbar \omega_i \left(\nu_i + \frac{1}{2} \right)$$

$$= \sum_i \hbar \lambda_i^{1/2} \left(\nu_i + \frac{1}{2} \right)$$

Quantum mechanical treatment of normal modes is valid within H.O. approximation. It assumes the molecule :

(1) doesn't rotate

(2) is an ideal harmonic oscillator (no anharmonicity).

Vibrational Energy Levels for H₂O

The vibration QNs of each modes are given in parentheses ($\nu_1, \nu_2, \dots, \nu_{3N-6}$)

In water we have (ν_1, ν_2, ν_3)

Fundamental levels : are levels with one $\nu_i = 1$ and all other ν_i 's = 0

e.g. (1, 0, 0) fundamental sym. str.

Overtone levels : are levels with one $\nu_i > 1$ and all other ν_i 's = 0

e.g. (0, 0, 1) fundamental antisym. str.

Combination levels : are levels with more than $\nu_i \neq 0$

Although combination levels exist, transitions among them is governed by symmetry rules.

The ground level (0, 0, 0) has the energy of:

$$\bar{E} = \sum_i^{3N-6} \frac{1}{2} h\nu_i \quad (\text{zero-point energy})$$

$$= (3900 + 3800 + 1600) \text{ cm}^{-1} / 2$$

$$= 4650 \text{ cm}^{-1}$$



$^{34}\text{S}^{16}\text{O}_2$: High-resolution analysis of the (030), (101), (111), (002) and (201) vibrational states; determination of equilibrium rotational constants for sulfur dioxide and anharmonic vibrational constants

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ABSTRACT

High resolution Fourier transform spectra of a sample of sulfur dioxide, enriched in ^{34}S (95.3%), were completely analyzed leading to a large set of assigned lines. The experimental levels derived from this set of transitions were fit to within their experimental uncertainties using Watson-type Hamiltonians. Precise band centers, rotational and centrifugal distortion constants were determined. The following band centers in cm^{-1} were obtained: $\nu_0(3\nu_2)=1538.720198(11)$, $\nu_0(\nu_1 + \nu_3)=2475.828004(29)$, $\nu_0(\nu_1 + \nu_2 + \nu_3)=2982.118600(20)$, $\nu_0(2\nu_3)=2679.800919(35)$, and $\nu_0(2\nu_1 + \nu_3)=3598.773915(38)$. The rotational constants obtained in this work have been fit together with the rotational constants of lower-lying vibrational states [W.J. Lafferty, J.-M. Flaud, R.L. Sams, EL Hadjiabib, J. Mol. Spectrosc. 252 (2008) 72–76] to obtain equilibrium constants as well as vibration–rotation constants. These equilibrium constants have been fit together with those of $^{32}\text{S}^{16}\text{O}_2$ [J.-M. Flaud, W.J. Lafferty, J. Mol. Spectrosc. 16 (1993) 396–402] leading to an improved equilibrium structure. Finally the observed band centers have been fit to obtain anharmonic rotational constants.

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1. Introduction

Recently the infrared spectrum of $^{34}\text{S}^{16}\text{O}_2$ has been the subject of a high resolution study [1] concerning the three fundamental bands, ν_1 , ν_2 and ν_3 , as well as the corresponding hot bands, $2\nu_2 - \nu_2$, $\nu_1 + \nu_2 - \nu_2$ and $\nu_2 + \nu_3 - \nu_2$. In addition, the $\nu_2 + \nu_3$ combination band was studied. In this paper, we present a high-resolution analysis of the $3\nu_2 - 2\nu_2$, $\nu_1 + \nu_3$, $\nu_1 + \nu_2 + \nu_3 - \nu_2$, $2\nu_3$, and $2\nu_1 + \nu_3$ bands. The molecular spectroscopic constants were derived by fitting the experimental energy levels of the (030), (101), (111), (002), and (201) vibrational states of $^{34}\text{S}^{16}\text{O}_2$. The rotational constants obtained in this work were fit together with those of Ref. [1] and a very accurate set of equilibrium rotational constants was obtained. These equilibrium constants were finally fit with those of $^{32}\text{S}^{16}\text{O}_2$ [2] and an improved equilibrium structure has been determined. The observed band centers have been fit to obtain anharmonic vibrational constants.

2. Experimental details

Numerous high-resolution spectra of a sulfur dioxide sample enriched in $^{34}\text{S}^{16}\text{O}_2$ (95.4%) covering the 19, 7–8, 5–6 and 3.3–

4 μm spectral regions were recorded using a Bruker Fourier transform spectrometer.¹ The wavenumber uncertainty of lines in all the regions studied was about $\pm 0.0002 \text{ cm}^{-1}$ for well isolated lines. The experimental details for all the bands studied including a table of the recording conditions have been given in a previous paper [1].

3. Analysis and results

For the $\nu_1 + \nu_3$ band, the analysis was started using the constants given in [3]. For all the remaining bands the analysis was conducted either by following distinctive line series or using predictions based on the analysis of the lower-lying bands [1]. Table 1 gives the range of observed energy levels for each state.² The upper state rotational levels were fit using an A-type Watson Hamiltonian written in the I^r representation [4] and the corresponding Hamiltonian constants are given in Table 2. In Table 1 we present also the statistical analysis of the results which show clearly the

¹ Certain commercial equipment instruments or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

² A list of assigned experimental lines can be obtained from the authors. The data have also been deposited in the archives of the journal.

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Table 1

Range of quantum numbers observed for the experimental energy levels and statistical analysis of the energy level calculation for the (030), (101), (002), (111), and (201) vibrational states of $^{34}\text{S}^{16}\text{O}_2$

Vibrational state	(030)	(101)	(002)	(111)	(201)
Number of levels	126	836	488	327	413
J_{max}	44	64	57	45	47
K_{max}	6	22	18	15	13
$0.0000 \leq \delta < 0.0002$	72.2%	61.5%	36.5%	48.6%	33.7%
$0.0002 \leq \delta < 0.0004$	20.6%	25.8%	28.3%	28.8%	22.0%
$0.0004 \leq \delta < 0.0019$	7.2%	12.7%	35.2%	22.6%	44.3%
Std. Devi, (10^{-3} cm^{-1})	0.25	0.29	0.48	0.35	0.58

$$\delta = |E_{\text{Obs}} - E_{\text{Calc}}|.$$

quality of both the experimental data and the fits. The very good agreement between observed and calculated spectra can also be observed through the comparisons performed for selected spectral regions (Figs. 1–3).

4. $^{34}\text{SO}_2$ equilibrium constants

In order to determine the equilibrium constants of $^{34}\text{SO}_2$ we have fit the accurate rotational constants derived in this work for the (030), (101), (002), (111) and (201) states as well as the constants determined earlier [1] for the (000), (010), (020), (100), (001), (110) and (011) states. The quality of the available data is variable and we have assigned a weight proportional to the inverse of the squares of the uncertainty for each datum. Each rotational constant was fit using an expansion of the form:

$$X_v = X_e - \sum_i \alpha_i^x (v_i + \frac{1}{2}) + \sum_{i < j} \gamma_{ij}^x (v_i + \frac{1}{2})(v_j + \frac{1}{2}) + \dots \quad (1)$$

The data used in the fitting are given in Table 3 and the values of the equilibrium constants and vibration–rotation interaction constants are given in Table 4. Note that these constants are fully consistent with those obtained previously for $^{34}\text{S}^{16}\text{O}_2$ [2]. With the set of rotational equilibrium constants obtained in this way and those obtained previously for $^{32}\text{S}^{16}\text{O}_2$ it proves possible to improve the

equilibrium structure of SO_2 . However, the constants derived from the fitting have first to be corrected for small contributions from electron–rotation interaction effects and from centrifugal distortion terms (Figs. 1–3).

The correction for the effect of electron–rotation interaction can be written as [5,6]

$$I_{\text{elect}}^z = -(m/M)I_z g_{zz} \quad (2)$$

Where m is the mass of the electron and M the mass of the proton. The molecular g_{zz} factors have been taken from the study of Burrus [7].

To take into account the centrifugal distortion corrections, we followed the method outlined in [4]. The rotational constants derived from the fitting given in Table 4 can be related to the actual constants through:

$$A_e = B_z^{(A)} = B_z^e + 16T_{004} - 2\tau_{xzxz} \quad (3)$$

$$B_e = B_x^{(A)} = B_x^e - 8(\sigma + 1)T_{004} - 2\tau_{xzxz} \quad (4)$$

$$C_e = B_y^{(A)} = B_y^e + 8(\sigma - 1)T_{004} + 3\tau_{xzxz} \quad (5)$$

$$\text{with } T_{004} = \frac{1}{16}(T_{xx} + T_{yy} - 2T_{xy}) \quad (6)$$

$$T_{xx} = -\Delta_J - 2\delta_J, T_{yy} = -\Delta_J + 2\delta_J, T_{zz} = -\Delta_J - \Delta_{JK} - \Delta_K \quad (7)$$

$$\text{and } \sigma = (2B_z^e - B_x^e - B_y^e)/(B_x^e - B_y^e) \quad (8)$$

T_{xy} was derived using planarity conditions:

$$T_{xy} = \frac{1}{2}(B_x^2 B_y^2) \left(-\frac{T_{zz}}{B_z^4} + \frac{T_{xx}}{B_x^4} + \frac{T_{yy}}{B_y^4} \right) \quad (9)$$

and τ_{xzxz} was estimated using:

$$\tau_{xzxz} = -16B_x B_y B_z / \omega_3^2 \quad (10)$$

Table 5 gives the corrected moments of inertia. These moments of inertia were least squares fit together with those previously obtained for $^{32}\text{S}^{16}\text{O}_2$ [2], leading to the equilibrium structural parameters:

$$r_e(\text{S}=\text{O}) = 1.4307932(40) \text{ \AA} \quad \text{and} \quad \angle_e(\text{O}=\text{S}=\text{O}) = 119.32898(24)^\circ.$$

Table 2

Vibrational band centers and rotational constants for the (030), (101), (002), (111) and (201) vibrational states of $^{34}\text{S}^{16}\text{O}_2$

	(030)	(101)	(002)	(111)	(201)
E_v	1538.720198(11) ^a	2475.828004(29)	2679.800919(0.35)	2982;118600(20)	3598.773915(38)
A	2.08707257(200)	1.948429485(700)	1.92878637(150)	1.986059608(860)	1.94863494(220)
B	0.344366871(370)	0.341402270(180)	0.341877125(200)	0.341471177(100)	0.339774427(210)
C	0.290624729(210)	0.289753669(140)	0.290084589(110)	0.2892184036(710)	0.288351064(150)
$\Delta_K \times 10^4$	1.099857(1500)	0.81255487(3800)	0.7894967(1400)	0.9002291(1200)	0.8218775(3600)
$\Delta_{JK} \times 10^5$	-0.4223388(1100)	-0.37974105(8500)	-0.4049918(2100)	-0.39676854(5900)	-0.37010870(8400)
$\Delta_J \times 10^6$	0.22049743(1700)	0.22117133(6400)	0.22397966(8000)	0.22148245(4000)	0.2205614(6900)
$\delta_K \times 10^6$	0.1409469(1200)	0.836844(1100)	0.706632(4100)	0.1020851(2400)	0.918387(4500)
$\delta_J \times 10^7$	0.58395256(9700)	0.5806223(5500)	0.5882873(4400)	0.5841908(2500)	0.5806814(5000)
$H_K \times 10^7$	0.9623(2800)	0.11202773(5800)	0.1059884(3100)	0.1389191(4400)	0.108277(1500)
$H_{KJ} \times 10^9$	-0.87 ^b	-0.544729(2300)	-0.50099(1400)	d	c
$H_{JK} \times 10^{11}$	0.67 ^b	c	c	d	c
$H_J \times 10^{12}$	c	0.41413(1300)	c	d	c
$h_K \times 10^9$	0.9 ^b	0.53402(1100)	c	d	c
$h_{KJ} \times 10^{13}$	c	c	c	d	c
$h_J \times 10^{12}$	c	0.19118(1100)	c	d	c
$L_K \times 10^{11}$	-0.48 ^b	c	c	d	c
$L_{KKJ} \times 10^{12}$	0.18 ^b	c	c	d	c
$L_{KJ} \times 10^{15}$	c	c	c	d	c
$L_{JK} \times 10^{17}$	c	c	c	d	c
$L_J \times 10^{18}$	c	c	c	d	c
$P_K \times 10^{15}$	0.82 ^b	c	c	d	c
$P_{KKJ} \times 10^{16}$	c	c	c	d	c
$P_{KJ} \times 10^{17}$	c	c	c	d	c

^a Uncertainties are 1σ .

(All the results are in cm^{-1}).

^b Extrapolated from (000),(010) and (020) values [1].

^c Fixed at ground state values [1].

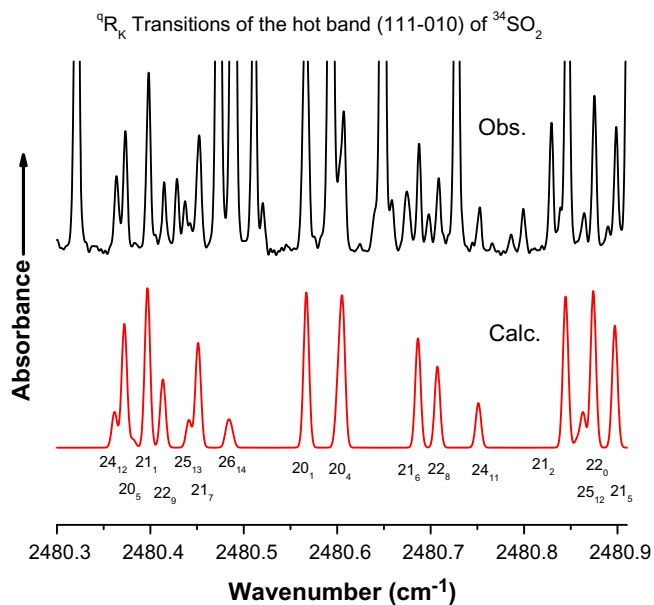
^d Fixed at (010) values [1].

Table 3
Observed and calculated rotational constants

	A		B		C	
	EXP	(O–C)*10 ⁶	EXP	(O–C)*10 ⁶	EXP	(O–C)*10 ⁶
000	1.967733713 ^a	0.26	0.3441883891	–0.22	0.2922455227	0.30
010	2.005731339	–0.59	0.3442590474	0.30	0.2917103888	–0.065
020	2.04547640	0.00	0.344318760	0.50	0.291170092	–0.16
100	1.96821909	–0.59	0.342551346	–1.54	0.290864145	–0.23
001	1.94814294	–0.59	0.343034313	1.94	0.291162785	–0.33
030	2.08707257	0.00	0.344366871	–0.29	0.290624729	0.098
110	2.006420332	1.04	0.342625774	2.75	0.2903419697	0.41
011	1.985576007	1.04	0.343099540	–2.97	0.2906143287	0.41
101	1.948429791	1.04	0.341402177	–0.74	0.289753504	–2.79
002	1.92878637	0.00	0.341877125	0.98	0.290084589	3.57
111	1.986059691	–1.63	0.341471193	–1.86	0.2892184057	–0.64
201	1.94863494	0.00	0.339774427	0.97	0.288351064	1.60

^a (All the results are in cm^{–1}).**Table 4**
³⁴S¹⁶O₂ Equilibrium rotational constants and vibration–rotation interaction constants

	A	B	C
X _e	58724.057(210) ^a	10359.2414(800)	8805.9516(110)
α ₁ ^a	–16.944(170)	49.1314(730)	41.186(100)
α ₂ ^a	–1095.343(390)	–2.4210(710)	15.832(120)
α ₃ ^a	582.757(240)	34.7569(610)	31.8348(850)
γ ₁₁ ^a	–1.1846(710)		
γ ₁₂ ^a	6.0260(810)		0.3583(730)
γ ₁₃ ^a	–6.0260(810)	0.1877(580)	–0.7789(610)
γ ₂₂ ^a	23.795(210)	–0.1592(200)	–0.0814(240)
γ ₂₃ ^a	–16.9993(820)		–0.4327(730)
γ ₃₃ ^a	3.4891(830)		
γ ₂₂₂ ^a	0.5281(360)		

^a Uncertainties are 1σ.
(All the results are in MHz).**Fig. 1.** Comparison of observed and calculated transitions of the a-type 111–010 hot band of ³⁴SO₂. Most of the transitions originating in the ground state of the band are off-scale. The lower-state rotational quantum numbers are given for each hot band line observed. The upper state quantum numbers can be obtained using ΔJ=+1, ΔK_a=0 and ΔK_c=+1.

5. Vibrational anharmonic constants

During the course of this work 11 vibrational energy levels have been determined. This permits us to make good estimates of the

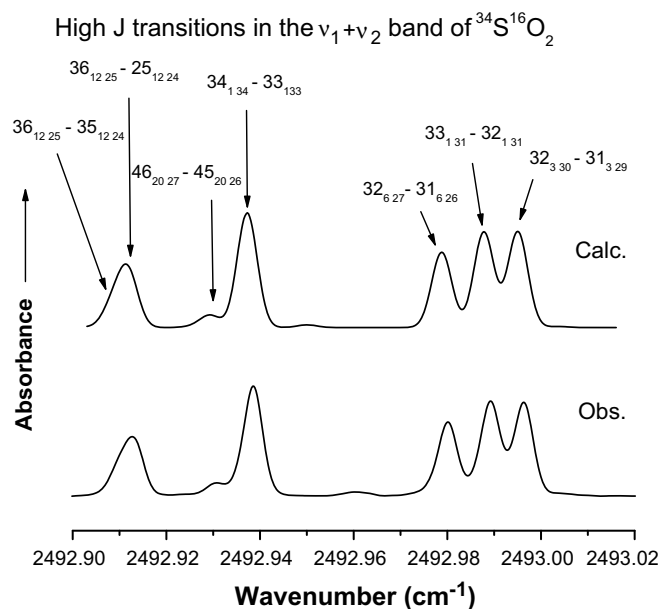
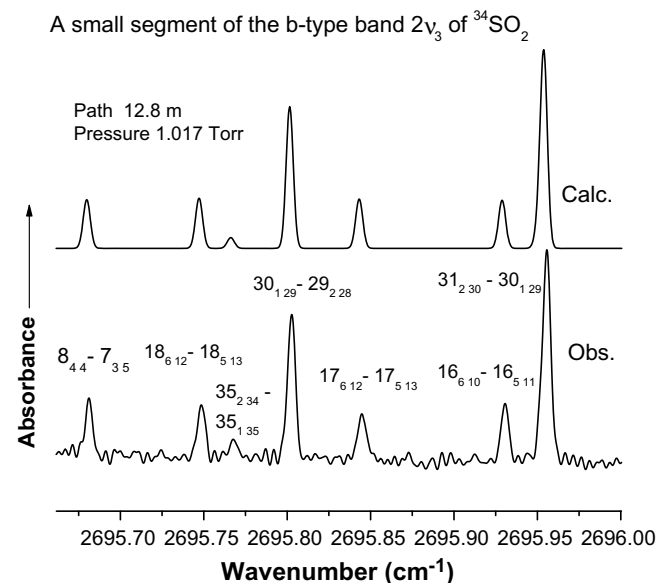
**Fig. 2.** Comparison of observed and calculated high J transitions in the a-type v₁ + v₂ band of ³⁴SO¹⁶O₂.**Fig. 3.** Comparison of observed and calculated spectra of a small portion of the weak b-type 2v₃ band of ³⁴SO¹⁶O₂.

Table 5
Moments of inertia of $^{34}\text{S}^{16}\text{O}_2$ in $\text{amu } \text{Å}^2$

	I_x^{fit}	ΔI_x^{elec}	ΔI_x^{cd}	I_x
I_A	8.605983(31) ^{a,b}	−0.00284	0.000014	8.603171(60) ^c
I_B	48.785336(77)	−0.003268	0.000961	48.783028(150) ^c
I_C	57.390.623(76)	−0.002313	−0.001641	57.386669(140) ^c

^a The value 505379.07 MHz/amu Å^2 has been used to convert the X_e rotational constants into the I_x^{fit} values.

^b Uncertainties are 1σ .

^c Estimated uncertainties.

Table 6
Vibrational harmonic and anharmonic constants of $^{34}\text{S}^{16}\text{O}_2$ in cm^{-1}

	Constant (unc)
ω_1^0	1148.3699(130) ^a
X_{11}	−3.8863(89)
ω_2^0	513.8656(90)
X_{22}	−0.3195(34)
ω_3^0	1350.2981(158)
X_{33}	−5.1985(87)
X_{12}	−3.206(10)
X_{13}	−13.760(11)
X_{23}	−4.040(10)
ω_1	1160.7366(200) ^b
ω_2	517.8043(120) ^b
ω_3	1364.3966(220) ^b

^a Uncertainties are 1σ .

^b Estimated uncertainties.

first order anharmonic constants. The eleven data were fit to the equation [8]:

$$G_0(v_1, v_2, v_3) = \omega_1^0 v_1 + \omega_2^0 v_2 + \omega_3^0 v_3 + X_{11} v_1^2 + X_{22} v_2^2 + X_{33} v_3^2 + X_{12} v_1 v_2 + X_{13} v_1 v_3 + X_{23} v_2 v_3 \quad (11)$$

The constants obtained from the fit are given in Table 6. The superscript 0 indicates that the expression is referred to the lowest vibrational state. Although the uncertainties given are one standard deviation, the data are so limited that they must be considered as estimates with the true error probably being several times larger. The ω_i , which are the zero-order frequencies referred to the mini-

mum of the potential curve, can be easily calculated (see Ref. [8]) and are also listed in Table 6.

6. Conclusion

An extensive analysis of the $^{34}\text{S}^{16}\text{O}_2$ spectrum was performed leading to the accurate determination of band centers, rotational and centrifugal distortion constants for the (030), (101), (111), (002) and (201) vibrational states of this molecule. Equilibrium rotational constants were derived, and an improved equilibrium structure has been obtained for sulfur dioxide.

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