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Microwave Rotational Spectral Study of SO₂-CO

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Abstract

The microwave spectrum of the molecular complex of sulfur dioxide (SO₂) with carbon monoxide (CO) has been studied with a pulsed-beam Fourier Transform Microwave Spectrometer (FTMW) from a pair of gas samples of 1 % by volume of SO₂ and CO in Ar, and introduced via separate capillary inputs to the flow nozzle. The frequency coverage was about 7 GHz to 16 GHz for various isotopomers. The molecular structure was determined with the aid of spectral studies of isotopically substituted monomers containing ¹³C, ¹⁸O and ³⁴S. The rotational analyses provide the rotational and centrifugal distortion constants for all of the isotopomers analyzed. The structure determination is compared to detailed *ab initio* structural calculations. The electric dipole moment components along the *a*- and *c*-axis were determined from Stark effect measurements.

Keywords

carbon monoxide; dimer; microwave spectrum; rotational spectrum; structure; sulfur dioxide

1. Introduction

Binary molecular complex structures have been the focus of many recent experimental and theoretical studies. These investigations of closed shell molecules range from moderately strong bonding of Lewis acids and bases, to hydrogen bonding interactions and weak bonding in van der Waals pairs. The development of the pulsed-beam, Fourier-transform microwave spectrometer by Balle and Flygare [1] has led to a wide range of molecular complex studies [2]. For many complexes containing the CO monomer, CO acts as an electron donor. For example, the C atom of CO hydrogen bonds to strong acids such as HCl, HF and HBr [3] as well as neutral or weak acids such as H₂O [4] and HCCH [5]. On the other hand complexes containing SO₂ show a variety in binding sites. With strong acids the sulfur dioxide O atom forms hydrogen bonds in SO₂—HF and SO₂—HCl [6] while many other partners interact perpendicular to the SO₂ plane, for example, this is the case with SO₂--HCCH [7].

2. Experimental Details

The rotational spectrum of SO₂-CO was observed using an early version of the Balle-Flygare [1] pulsed nozzle Fourier Transform Microwave (FTMW) spectrometer at NIST [8,9] in 1990. The complex was formed through supersonic expansion from a pulsed solenoid valve employing two capillary input lines (see Fig. 1) with Ar gas seeded with 1 % by volume of SO₂ in one inlet and Ar gas seeded with 1 % by volume of CO in the second inlet with mass flow controllers feeding each inlet, and maintaining a slow flow by pumping out of the top of the solenoid valve. The microwave pulse was of 0.5 μ s duration and the expansion was through a 0.5 mm diameter nozzle located perpendicular to the microwave propagation through the Fabry-Perot cavity. Stagnation pressures ranged from 120 kPa to 150 kPa and the rotational temperature of the molecular expansion gas was on the order of 1 K. Typically, data from 100 to 1000 nozzle pulses were averaged to obtain a reasonable signal to noise ratio. Further details of the typical spectrometer operation can be found in Refs. [8,9]. All gases were obtained from commercial sources.

3. Spectral Observations

a. Spectral Assignment and Analysis

Since no theoretical structure of the dimer was available at the time of our initial experiments, the spectral survey was guided by an estimated structure, whereby the C atom of CO binds to the S atom of SO₂ perpendicular to the plane of SO₂ at the sum of the van der Waals radii of 3.50 Å by employing the commonly used values of 1.70 Å for carbon and 1.80 Å for sulfur from Bondi [10]. This estimated structure provided rotational constants of $A = 8820$ MHz, $B = 1427.5$ MHz and $C = 1280.4$ MHz with the S—CO atoms lying in the a -, c -plane. Since the μ_c dipole component was expected to be largest, approximating the SO₂ dipole moment of $5.4474(3) \times 10^{-30}$ C m (1.63308(8) D) [11], the $1_{10} - 0_{00}$ transition was sought initially near 10.1 GHz. Once several c -type transitions were assigned with the aid of their Stark effect shifted components, a number of the weaker a -type transitions were located. The assigned transitions are shown in Table 1. Subsequently, the ³⁴SO₂-CO isotopomer was observed with natural abundance ³⁴S and SO₂-¹³CO from a sample enriched in ¹³C with the assigned transitions also shown in Table 1. In order to augment the structural determination, samples enriched in ¹⁸O were employed to obtain the spectra of SO₂-C¹⁸O and S¹⁸O₂-CO which are listed in Table 2. The rotational analyses were carried out by using a rigid rotor Hamiltonian written with a Watson S-reduction set of rotational and centrifugal distortion constants [12]. The rotational analysis results for the 5 isotopomers are listed in Table 3.

b. Dipole moment determination

Stark effect measurements were carried out on three c -type transitions of SO₂-CO: the $1_{11} - 1_{01}$ $M = 1$, $1_{10} - 0_{00}$ $M = 0$, and $2_{11} - 1_{01}$ $M = 0, 1$ transitions. The flow nozzle was located perpendicular to the direction of microwave propagation between the mirrors and symmetrically above the 25 cm $\times$ 25 cm parallel Stark plates at a separation of about 26 cm, giving the selection rule $M = 0$. The plates are located equidistant from each mirror. Calibration of the effective plate spacing is accomplished with Stark-shifted measurements

on the $J=1-0$ transition of OCS and the known dipole moment of $2.3856(10) \times 10^{-30}$ C·m (0.71519(3) D) [13]. In order to minimize the non-uniformity of the electric field, +V and -V voltages are applied to the two plates. Frequency shifts of up to 1.4 MHz were measured on 11 Stark components to derive the dipole moment components $\mu_a = 1.069(3) \times 10^{-30}$ C·m (0.3205(5) D) and $\mu_c = 5.227(10) \times 10^{-30}$ C·m (1.567(3) D) where uncertainties are Type A with coverage factor $k = 2$ (2 standard deviations) [14].

4. Structure Calculations

A comparison of the I_{bb} moment of inertia of SO₂ and the dimer second moment of inertia, P_{bb} , listed in Table 4 shows that only the two O atoms of SO₂ do not lie in the a,c -plane and must have symmetric b -coordinates with respect to the a,c -plane. In addition, from the dipole moment analysis it is clear that the symmetry axes of the two monomers lie in the a,c -plane. As is commonly done in structural calculations for molecular complexes, we assume that the monomer geometry does not change in forming the dimer. With this assumption and the fact that the S atom and CO unit lie in the a,c -symmetry plane, only three parameters are needed to define the structure: the centers-of-mass distance, R_{cm} , and the two angles, θ and ϕ , shown in Fig. 2.

The structure fitting routine used was STRFTQ, written by Schwendeman [15], which allows the moments-of-inertia for multiple isotopomers to be fit simultaneously to any of the internal coordinates defined on input. The structure was parameterized in the internal coordinates as developed by Thompson [16], where each atom is specified by its orientation with respect to the previously defined two or three atoms. As usual with fitting dimer structures, the individual molecule internal coordinates were fixed at their monomer r_0 values. For SO₂ we used $r_0 = 1.432$ Å and $\angle\text{OSO} = 119.54^\circ$ derived here and for CO we used $r_0 = 1.131$ Å [17]. The rotational constants, A and B , for all of the isotopomers shown in Table 3 were used to derive the I_a and I_b moments of inertia employed in the fit. Since we found that the two angles, θ and ϕ , were highly correlated and caused poor convergence in the fits, we fit two of the three parameters, R_{cm} and θ , and fixed the value of ϕ at various values near 180° to locate the smallest residual in the moment of inertia calculated values. The fit values are listed in Table 4 and compared to the theoretical calculated structure as described in the next section.

Since we have moment of inertia data for each atom of the dimer singly or doubly substituted, a complete substitution structure can be calculated from the usual Kraitchman analysis [18] or Chutjian analysis [19] in the case of double substitution for ¹⁸O in SO₂. In Table 6 we list the a , b , and c -coordinates derived from the substitution (r_s) analysis and compare these with the coordinates determined in the r_0 least squares fit described above. Note that the b -coordinate of only the O atoms of SO₂ should be non-zero, while the Kraitchman analysis give an imaginary value for the S atom and small non-zero values for the C and O atoms of CO. Surprisingly, the a -coordinates show larger deviations than one usually finds in rigid molecules.

Further information regarding the fitted structure may be obtained from the derived dipole moment components. Using the angles defined in Fig. 2, the dipole moment components may be expressed as follows using the monomer dipole moments:

$$\mu_a = \mu_0(\text{SO}_2)\cos\theta + \mu_0(\text{CO})\cos\varphi + \mu_{\text{induced}} \quad (1)$$

$$\mu_c = \mu_0(\text{SO}_2)\sin\theta + \mu_0(\text{CO})\sin\varphi + \mu_{\text{induced}} \quad (2)$$

If one assumes the induced moment is small, then the components can be calculated from the known monomer ground state dipole moments of $5.4474(3) \times 10^{-30}$ C·m (1.63308(8) D) [11] for SO₂ and $0.36625(20) \times 10^{-30}$ C·m (0.10980(6) D) [20]. The resulting components are $\mu_a = 1.23 \times 10^{-30}$ C·m (0.37 D) and $\mu_c = 5.20 \times 10^{-30}$ C·m (1.56 D), both in reasonable agreement with the measured values listed in Table 5. It should be noted that for μ_a the contributions from the two monomers are opposite in sign and only the SO₂ moment contributes to μ_c .

5. Theoretical Calculations

The SO₂-CO geometry and vibrational frequencies were calculated at the CCSD(T*)-F12a level of theory (explicitly correlated coupled cluster with scaled triples) [21] as implemented in the MOLPRO 2012.1 quantum chemistry software [22,23]. These F12 calculations are expected to be closer to the complete basis set limit [21] than the conventional CCSD(T) calculations previously reported by Budzák et al. [24]. Equilibrium geometries were optimized using the cc-pVxZ-F12 (X=D,T,Q) family of basis sets developed by Peterson and co-workers [25]. The equilibrium geometry obtained with the cc-pVDZ-F12 basis is nearly in the complete basis set limit; geometric parameters calculated using the larger cc-pVTZ-F12 and cc-pVQZ-F12 bases differed by no more than 0.01 Å for bond lengths and 1° for angles. (All computed geometries and electronic energies can be found in the Supporting Information)

The (anharmonic) vibrationally averaged 0 K geometry was computed at the CCSD(T*)-F12a/cc-pVDZ-F12 level of theory using vibrational configuration interaction theory [26] up to quadruple excitations and two-mode couplings (2M-VCISDTQ, “ZPVE” macro in MOLPRO. This geometry is illustrated in Figure 3, and the geometric parameters are listed in Tables 5 and 6. The calculated parameters for the geometry of the SO₂ monomer (R(S-O), <OSO) and the distance between the two monomers (R_{cm}) agree with the structural fit to within 0.015 Å and 0.5°. The computed C-O distance (1.105 Å) is shorter than both the value used in the structural fit (1.131 Å) and the computed CCSD(T*)-F12a/cc-pVDZ-F12 bond length of the CO molecule ($r_e=1.132$ Å).

The calculated relative orientation of the two monomers (θ , φ) is significantly different from the structural fit. In the structural fit, the SO₂ C₂ axis is not perpendicular to R_{cm} ($\theta=80.9^\circ$), and the C-O axis is collinear with R_{cm} ($\varphi=180^\circ$). In the computed geometry, the SO₂ C₂ axis is perpendicular to R_{cm} ($\theta=90.3^\circ$), and the C-O axis is not collinear with R_{cm} ($\varphi=164^\circ$). Our

computed orientation of the two monomers agrees with the equilibrium geometry calculated by Budzák et al. [24] to within 1°, as shown in Table 5.

6. Discussion

While the results reported here are the first published experimental data on OC—SO₂, there are two unpublished PhD thesis studies employing a tunable-diode-laser coupled with a molecular beam spectrometer and molecular beam electric resonance (MBER) method. In the first study by C. H. Hwang [19] the infrared spectrum of OC—SO₂ was measured and yielded rotational constants for the excited state of $A' = 8839.40(282)$ MHz, $B' = 1499.46(109)$ MHz and $C' = 1332.87$ MHz. These values are reasonably close to the ground state constants given in Table 3, with the B and C values within 5 MHz and 1 MHz, respectively. The MBER study by Cheng [20] provided a determination of the dipole moment components $\mu_a = 1.06859(2) \times 10^{-30}$ C·m (0.320355(6) D) and $\mu_c = 5.20016(13) \times 10^{-30}$ C·m (1.55897(4) D). The μ_a value is in excellent agreement with our determination, although the present result is less precise. However the μ_c values do not agree within the quoted uncertainty, but differ by $0.027(11) \times 10^{-30}$ C·m (0.008(3) D) which is about 2.5 times the uncertainty. The source of this discrepancy is uncertain, however, the MBER results were obtained at high electric fields and required full matrix diagonalization to fit to experimental accuracy, while our results are in the weak field region and employ Stark coefficients calculated with the full set of rotational and centrifugal distortion constants determined here.

The discrepancy between the calculated and experimental orientation of monomers may be due to the flatness of the SO₂-CO potential energy surface. The complex has two vibrational modes with harmonic frequencies less than 30 cm⁻¹ (calculated at CCSD(T*)-F12a/cc-pVxZ-F12, x=D or T). Furthermore, the difference in electronic energies between the experimental geometry (r_0) and the quantum chemistry optimized geometry is 1 kJ/mol (calculated at CCSD(T*)-F12a/cc-pVxZ-F12, x=D, T, or Q). The SO₂-CO complex may sample enough of the potential energy surface to yield a different experimental geometry than the calculated energetic minimum geometry.

Among the SO₂ dimeric complexes previously reported, only SO₂-N₂ [29] and SO₂-NCH [30] are found to exhibit similar structures to the SO₂-CO. Each have the N atom directed toward the SO₂ plane and the symmetry axis of the N₂ and HCN lying near the a -axis of the complex. Perhaps this is a result of the fact that CO, N₂ and HCN are isoelectronic, and thus might show similar binding properties in forming molecular complexes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com).

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Fig. 1.
Flow nozzle design

Fig. 2.
Structural parameters

Fig. 3.
Final fitted and theoretical structures

Table 1

Microwave spectrum of SO₂-CO, ³⁴SO₂-CO, and SO₂-¹³CO.

J'	K'_a	K'_c	J''	K''_a	K''_c	SO ₂ -CO Frequency ^a MHz	O-C ^b kHz	³⁴ SO ₂ -CO Frequency ^a MHz	O-C kHz	SO ₂ - ¹³ CO Frequency ^a MHz	O-C ^b kHz
2	2	0	-	2	1	2.6724(9) ^c	0.6				
1	1	0	-	1	1	163.4870(6) ^c	-0.1				
1	1	1	-	1	0	7373.434(4)	-0.1	7351.367	0	7386.348	7
6	0	6	-	5	1	8118.832(4)	0.4				
3	1	3	-	2	1	8234.962(4)	-0.1				
3	0	3	-	2	0	8472.254(4)	0.9	8399.186	1		
3	2	2	-	2	1	8478.178(4)	-0.7				
3	2	1	-	2	0	8488.859(4)	-1.2				
3	1	2	-	1	1	8725.252(4)	0.2				
4	2	3	-	5	1	9464.327(4)	1.4				
3	2	1	-	4	1	10256.461(4)	0.3				
7	0	7	-	6	1	10330.119(4)	0.3				
1	1	0	-	0	0	10364.800(4)	1.1	10314.430	1	10335.455	-14
4	0	4	-	3	0	11283.096(4)	1.1	11186.225	0		
3	2	2	-	4	1	11877.248(4)	0.7				
2	1	1	-	1	0	13355.178(4)	-0.3	13276.530	-2	13283.615	7
2	2	0	-	3	1	13397.248(4)	-0.7				
5	0	5	-	4	0	14082.694(4)	-0.5				
2	2	1	-	3	1	14375.290(4)	-1.7				
3	1	2	-	2	0	16427.521(4)	0.0	16318.682	1	16311.452	0

^aUncertainties for NIST measurements are estimated to be 4 kHz for all NIST measurements and refer to the last digit shown. These are Type B, coverage factor $k=2$ [14].

^bObserved minus calculated value.

^cFrom M.-S. Cheng PhD thesis, ref. [28].

Table 2

Microwave spectrum of S¹⁸O₂-CO, and SO₂-C¹⁸O.

J'	K'_a	K'_c	-	J''	K''_a	K''_c	$S^{18}O_2$ -CO Frequency ^a MHz	O-C ^b kHz	SO ₂ -C ¹⁸ O Frequency ^a MHz	O-C ^b kHz
3	2	1	-	4	1	3	7807.172	0.1	11196.436	0.2
3	0	3	-	2	0	2	8269.602	0.2	8000.532	-0.7
1	1	0	-	0	0	0	9420.878	1.0	10272.439	1.0
7	0	7	-	6	1	5	10510.787	0	-	-
2	2	0	-	3	1	2	10930.479	-0.2	14146.978	-0.4
4	0	4	-	3	0	3	11008.787	0.2	10656.867	1.4
2	2	1	-	3	1	3	11962.910	0.1	15019.204	0.2
3	2	2	-	4	1	4	-	-	12642.837	0.1
2	1	1	-	1	0	1	12358.648	-1.5	13087.154	-0.9
5	0	5	-	4	0	4	13733.314	-0.2	13304.257	-0.4
3	1	2	-	2	0	2	15385.602	0.5	15974.833	-0.1

^aUncertainties are estimated to be 4 kHz for all measurements. These are Type B, coverage factor $k=2$ [14].

^bObserved minus calculated value.

Table 3

Rotational parameters of the SO₂-CO isotopomers.

Parameter	SO ₂ -CO	³⁴ SO ₂ -CO	SO ₂ - ¹³ CO	S ¹⁸ O ₂ -CO	SO ₂ -C ¹⁸ O
<i>A</i> (MHz)	8869.3736(16) ^a	8833.144(6)	8861.163(21)	7951.7550(26)	8864.873(3)
<i>B</i> (MHz)	1495.6986(5)	1481.547(3)	1474.579(11)	1469.3744(7)	1407.8169(17)
<i>C</i> (MHz)	1332.2055(4)	1321.842(5)	1315.505(120)	1292.1603(5)	1262.0607(13)
<i>D_J</i> (kHz)	6.587(10)	6.40(7)	<i>b</i>	6.285(13)	5.94(2)
<i>D_K</i> (kHz)	202.31(8)	196.8(23)	<i>b</i>	193.83(16)	182.24(19)
<i>D_K</i> (kHz)	-160.7(4)	<i>b</i>	<i>b</i>	-163.4(6)	-139.1(9)
<i>d_J</i> (kHz)	-0.753(4)	<i>b</i>	<i>b</i>	-0.781(6)	-0.68(6)
<i>d₂</i> (kHz)	-0.345(7)	<i>b</i>	<i>b</i>	0	-0.34(11)
Number ^c	20	6	4	10	10
rms (kHz)	1.2	2.3	15.6	1.1	1.5
Weighted rms ^d	0.31	0.58	3.9	0.28	0.38

^aNumbers in parentheses are two standard deviation uncertainties (Type A, coverage factor *k* = 2 [14]) and apply to the last digit(s).

^bFixed at value for the normal isotopic species.

^cNumber of rotational transitions treated for each conformer

^dUnitless root-mean-square deviation of the fit.

Table 4

Moment of inertia comparisons between SO₂ and SO₂-CO.

Isotopomer	$I_b(\text{SO}_2)$ (uÅ ²)	$P_{bb}(\text{dimer})$ (uÅ ²)
³² SO ₂ -CO	48.9808	49.2235
³² SO ₂ -C ¹⁸ O	48.9808	49.2346
³² SO ₂ - ¹³ CO	48.9808	49.2382
³⁴ SO ₂ -CO	48.9808	49.2137
³² S ¹⁸ O ₂ -CO	55.1101	55.3512

Table 5
Structural fit of 5 isotopomers for SO₂-CO and dipole moments compared to theoretical values.

Parameter	Fit Value ^a	Theory Value ^c	Budzák et al. ^d
R_{cm}	4.0586(11) ^b	4.046 Å	4.046 Å
Θ	80.9(32)°	90.3°	90.8°
ϕ	180(3)°	164°	165°
μ_a	1.069(3) × 10 ⁻³⁰ C·m 0.3205(5) D	1.32 × 10 ⁻³⁰ C·m 0.395 D	
μ_c	5.227(10) × 10 ⁻³⁰ C·m 1.567(3) D	5.69 × 10 ⁻³⁰ C·m 1.71 D	
Derived Value			
$R(\text{S}-\text{C})$	3.487(20) Å	3.44 Å	3.42 Å
$\angle \text{SCO}$	174.1(8)°	193°	191°

^a Assumed values for monomers: $r(\text{CO}) = 1.131$ Å, $r(\text{SO}) = 1.432$ Å, and $\angle \text{OSO} = 119.54^\circ$ (see text).
^b Uncertainties are Type A coverage factor $k = 2$ [14].
^c CCSD(T*)-F12a/VDZ-F12, vibrationally averaged geometry (2M-VCISDTQ). Values for monomers: $r(\text{CO}) = 1.105$ Å, $r(\text{SO}) = 1.431$ Å, and $\angle \text{OSO} = 119.9^\circ$.
^d Ref. [24]: CCSD(T)/aug-cc-pVTZ, equilibrium geometry. Values for monomers: $r(\text{CO}) = 1.135$ Å, $r(\text{SO}) = 1.455$ Å, and $\angle \text{OSO} = 118.1^\circ$.

Table 6

Structure Coordinates for SO₂-CO (Å)

Atom	Parameter	a	b	c
S	r_s^a	-1.236(1) ^b	0.071i	0.354(4) ^b
	$r_0(I_{a,b})^c$	-1.293	0.0	0.351
	r_{theory}^e	-1.231	0.0	0.350
O(SO ₂)	r_s^d	-1.209	1.238	-0.340
	$r_0(I_{a,b})^c$	-1.177	1.237	-0.361
	r_{theory}^e	-1.231	1.239	-0.367
C	r_s^a	2.199(8) ^b	0.123(146) ^b	0.196(91) ^b
	$r_0(I_{a,b})^c$	2.177	0.0	0.009
	r_{theory}^e	2.207	0.0	0.189
O(CO)	r_s^a	3.277(5) ^b	0.076(20) ^b	0.099(15) ^b
	$r_0(I_{a,b})^c$	3.308	0.0	0.013
	r_{theory}^e	3.271	0.0	-0.109

^aCostain rule, Kraitchman substitution [18], using signs from *40* fit.

^bUncertainties are Type A coverage factor $k = 2$ [14].

^cBased on fit results of Table 5.

^dChutjian double substitution [19].

^eCCSD(T*)-F12a/VDZ-F12, vibrationally averaged geometry (2M-VCISDTQ)