

# Critical Survey of the Molecular Structure Determination by the Use of Spectroscopic Data for SO<sub>2</sub>

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The equilibrium structure of the SO<sub>2</sub> molecule was calculated on the basis of the second-order approximation, using recent accurate spectroscopic data. The effects of Fermi and Darling-Dennison resonance were eliminated from the rotational constants of the excited vibrational states by the use of constrained least-squares. This resulted in  $r_e = 1.43080(1)$  Å and  $\theta_e = 119.329(2)^\circ$ , which are the most accurate values of bond distances and bond angles reported for triatomic molecules. The inertia defect,  $\Delta_c = -0.00027(143)$  amu Å<sup>2</sup>, was reduced perfectly to zero within its standard deviation, as required by the theory.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Molecular spectroscopy and electron diffraction are most powerful methods for molecular structure determination. The source of information for the former is the rotational constants obtained by the analysis of either infrared or microwave spectra. In contrast to electron diffraction, the application of spectroscopic techniques is rather limited to simple molecules, but it has a merit in giving accurate bond distances and bond angles. In this article we discuss the limits of accuracy of the results obtained and examine the precautions necessary for arriving at accurate results.

## Calculation procedure

Since a molecule always vibrates about its equilibrium position, even in the ground state, we should eliminate vibrational effects in order to obtain the structure at the equilibrium position. The rotational constants are usually expanded in vibrational quantum numbers to the second order:

$$A(\nu_1, \nu_2, \nu_3) = A_e - \sum_i (1/2)\alpha_i(\nu_i + 1/2)$$

$$+ \sum_{ij} (1/4)\gamma_{ij}(\nu_i + 1/2)(\nu_j + 1/2). \quad (1)$$

The  $A_e$ , and similarly  $B_e$  and  $C_e$ , are thus obtained by combining a set of rotational constants of nine or more vibrational states for a triatomic molecule. This is a formidable restriction for applying the procedure, because such a complete set of data is rarely available. The SO<sub>2</sub> molecule is one of the most fortunate cases: the vibration-rotation spectra have been precisely analysed for ten vibrational states by the efforts of many spectroscopists.<sup>1-4</sup>

When we want to make use of data obtained by different observers, precautions should be taken for the proper treatment of the data. First to be mentioned is the difference between the rotational constants obtained by the infrared analysis and those obtained by the microwave technique. From microwave spectra we obtain the rotational constants of a vibrational state, while the infrared method yields the difference between the rotational constants of the upper state in a transition and those of the ground or other lower state. This means that the rotational constants obtained by the latter method always depend on the rota-

Table 1. Rotational constant increments for vibrational states of SO<sub>2</sub> in the Nielsen approximation (in MHz).<sup>a</sup>

State	A	B	C	Ref.
(100)	32.8173(76)	-49.8827(29)	-42.3533(29)	3
(010)	1176.2487(87)	2.3086(41)	-15.8354(40)	1, 2
(001)	-620.4991(41)	-34.9137(31)	-32.9290(30)	3
(200)	63.4572(1540)	-99.5264(290)	-84.4691(261)	4
(020)	2407.1121(450)	4.1084(94)	-31.6650(89)	2
(002)	-1233.7331(1020)	-70.0887(159)	-65.7213(160)	4
(110)	1215.3292(2400)	-47.4440(412)	-57.8053(452)	4
(101)	-595.2052(197)	-84.6140(37)	-76.1287(37)	4
(011)	536.6789(318)	-32.6802(48)	-49.2137(46)	3
(030)	3696.9729(2402)	5.9411(208)	-47.9259(676)	4
	A(000)	B(000)	C(000)	
	60778.5270(29)	10317.9370(13)	8799.8485(13)	1

<sup>a</sup>The uncertainties in the last digits (one standard deviation) are given in parentheses after each value.

tional constants of the ground or lower state assumed for the analysis. In order to avoid irregularities due to the choice of the individual observers for the rotational constants of the reference state, we started the present calculations with rotational constant increments,  $A(v_1, v_2, v_3) - A(0, 0, 0)$ , etc., rather than with rotational constants themselves. The rotational constant increments we used are summarized in Table 1. They were initially transformed to the Nielsen approximation<sup>5</sup> by the procedure described in the Appendix (*vide infra*).

The rotational constants for the (200), (002), (110), (101) and (030) states were obtained by a critical re-analysis of the previous microwave re-

sults.<sup>4</sup> In order to calculate the increments, we used the rotational constants of the (000) state reported by Helminger and De Lucia.<sup>1</sup>

(I)  $\alpha_i$  and  $\gamma_{ij}$  constants. We calculated the  $\alpha_i$  and  $\gamma_{ij}$  constants by least-squares treatment of the ten sets of rotational constant increments listed in Table 1. In this process we eliminated surplus contributions due to Fermi resonance as well as those due to Darling-Dennison resonance,<sup>6</sup> as will be described in the next paragraph. The results are shown in Table 2.

(II) Elimination of the Fermi and Darling-Dennison Resonance Contributions. The rotational con-

Table 2.  $\alpha_i$  and  $\gamma_{ij}$  constants for SO<sub>2</sub> with the effects of Fermi and Darling-Dennison resonances eliminated (in MHz).

	A	$\sigma^D$ <sup>a</sup>	B	$\sigma^D$	C	$\sigma^D$
$\alpha_1$	-35.486	1.973	50.364	0.511	42.434	0.220
$\alpha_2$	-1127.855	1.310	-2.598	0.342	15.778	0.173
$\alpha_3$	614.954	1.049	34.824	0.279	32.573	0.123
$\gamma_{11}$	-2.208	0.772	0.409	0.201	0.382	0.080
$\gamma_{22}$	28.216	0.210	-0.145	0.052	0.010	0.033
$\gamma_{33}$	2.277	0.510	0.397	0.116	0.556	0.051
$\gamma_{12}$	-1.866	2.396	-0.018	0.564	0.346	0.274
$\gamma_{13}$	-0.008	0.215	1.263	0.077	0.128	0.034
$\gamma_{23}$	-18.769	0.331	-0.114	0.094	-0.514	0.041

<sup>a</sup> $\sigma^D$  denotes the standard deviation obtained by least-squares.

stants of higher vibrational states are influenced by various interactions which are not taken into account in Nielsen's second-order expression for the vibrating rotor. Therefore, these interaction effects should be eliminated before the rotational constants are applied for calculating the  $\alpha_i$  and  $\gamma_{ij}$  constants. Among these various interactions, Fermi resonance is the strongest and should be considered first.

The details of the calculation of Fermi resonance contributions are not described in this article but the principle applied is as follows: as Fermi resonance is directly connected with the cubic force constants, a tentative set of force constants was first assumed and the Fermi resonance contributions were calculated and subtracted from the rotational constant increments. By using the corrected increments the  $\alpha_i$  and  $\gamma_{ij}$  constants were evaluated, and on the basis of these  $\alpha_i$  constants the force constants of the molecule were calculated. The force constants thus obtained were used to calculate the resonance contributions in the second cycle. Iterations were carried out until the assumed force constants coincided with the force constants thus obtained. The final Fermi resonance contributions are shown in Table 3. It should be noted that the Fermi resonance contributions are of the same order of magnitude as, or sometimes larger than, those of the  $\gamma_{ij}$  constants. They are definitely

greater than the standard deviations of the rotational constant increments.

The Darling-Dennison effect was also treated in the same way. It affects only the (200) and (002) states and is weaker than the Fermi terms, but it is still of the same order of magnitude as the standard deviations of the rotational constant increments.

In the iteration process described above, the Fermi and the Darling-Dennison resonances were treated as "constraints" in the least-squares calculation of  $\alpha_i$ 's and  $\gamma_{ij}$ 's from the rotational constant increments. When the constraints are released, the deviations of unknown constants will increase: that is, their standard deviations will increase relative to those obtained by the constrained least-squares, probably by a factor of two or three. Accordingly, the standard deviations of physical quantities derived from the  $\alpha_i$ 's or  $\gamma_{ij}$ 's would also increase similarly.

(III) *Rotational constants and moments of inertia of the equilibrium configuration.* Having obtained the  $\alpha_i$  and  $\gamma_{ij}$  constants, the rotational constants of the equilibrium configuration are easily calculated from those of the ground state by the use of eqn. (1). Corresponding moments of inertia were calculated from:

$$I_c(A) = h/8\pi^2A, \quad (2)$$

for three rotational constants,  $A$ ,  $B$  and  $C$ . Corrections were made for the contributions due to electronic interactions, which were computed with  $g$ -factors reported by Pochan, Stone and Flygare.<sup>7</sup> The final moments of inertia to be used for the calculation of the molecular geometry are listed in Table 4.

(IV) *Molecular geometry,  $r_e$  and  $\theta_e$ .* A simple least-squares fit to the three components of the moment of inertia gave the bond distance  $r_e$  and bond angle  $\theta_e$ , as shown in Table 4.

(V) *Standard deviations.* The standard deviations of the physical quantities are calculated at each step of the computations. In deriving a quantity from known parameters by mathematical relation, variances were calculated by the law of error propagation, using the standard deviations of the initial quantities (we designate the results as  $\sigma^p$ ). When a least-squares calculation

Table 3. Contributions of Fermi and Darling-Dennison resonances to the rotational constant increments (in MHz).

State	A	B	C
Fermi resonances			
(100)	2.6839	-0.9578	-0.9202
(010)	2.2723	0.0469	0.0101
(001)	-0.7112	-1.4581	-1.2746
(200)	7.6069	-2.4938	-2.3671
(020)	2.9629	0.0081	-0.0218
(002)	1.2871	-3.9718	-3.5244
(110)	13.0940	-0.7444	-0.8767
(101)	-5.5433	-3.4964	-3.1593
(011)	1.2679	-1.3544	-1.2034
(030)	3.6954	-0.0792	-0.0890
Darling-Dennison resonances			
(200):(002)	0.4310	-0.0098	-0.0062

Table 4. Rotational constants, moments of inertia and the molecular structure of SO<sub>2</sub> in the equilibrium configuration.

	A	B	C
Rotational constants/MHz	60502.423(953)	10358.784(257)	8845.014(116)
Electronic moments of inertia/amu Å <sup>2</sup>	0.002747(2)	0.003085(58)	0.002745(61)
Moments of inertia corrected/amu Å <sup>2</sup>	8.35029(15)	48.78440(126)	57.13442(86)
Inertia defect/amu Å <sup>2</sup>	-0.00027(143)		
$r_e/\text{Å}$	1.43080 ( $\sigma^P = 1$ )		
$\theta_e/^\circ$	119.329 ( $\sigma^P = 2$ )		

was performed the standard deviations were calculated as usual, i.e. by their deviations from the observed values (we designate them as  $\sigma^D$ ). For comparison, the  $\sigma^P$ 's were also calculated using the standard deviations of the initial rotational constant increments, and the larger one for  $\sigma^D$  and  $\sigma^P$  was taken as an error limit estimate. As it can be discussed as to whether the error limit should be taken as  $2\sigma$  or  $3\sigma$ , "one sigma" is simply given throughout this article.

It is noted here that the errors in Planck's constant and in Avogadro's number were also taken into account in the error estimate for the moments of inertia. However, errors in these constants give no contributions to the standard deviation of the inertia defect, since the inertia defect is extremely small owing to cancellation of the three components.

(V) *Correlations.* In order to evaluate exactly the error limits for the final results, we should take into account correlations between the spectro-

scopic constants. Besides correlations due to the mathematical relations used in the calculations, there are correlations which arise from the fact that the rotational constants  $A$ ,  $B$  and  $C$  are not directly observable quantities but are derived simultaneously from the spectroscopic frequencies observed for a vibrational state. Fortunately, however, the mathematical relationships of  $\alpha_i$ 's and  $\gamma_{ij}$ 's to the rotational constant increments are separated for each of  $A$ ,  $B$  and  $C$ , so that the correlation factors between  $A$  and  $B$ ,  $A$  and  $C$ , or  $B$  and  $C$  have no effect on the final sigma values.

On the other hand, in the least-squares calculation of  $r_e$  and  $\theta_e$  from the three components of the moments of inertia, these correlations should be taken into account. It turned out, however, that the correlations due to this origin have no appreciable influence on the standard deviations of  $r_e$  and  $\theta_e$ . We have therefore neglected them in this report.

Table 5. Comparison of the equilibrium structure obtained using different approximations.

	Simple Watson approximation	Simple Nielsen approximation	Nielsen approximation corrected for Fermi and DD resonances
$A_e/\text{MHz}$	60501.728(1449)	60501.702(1514)	60502.423(953)
$B_e/\text{MHz}$	10359.244(10)	10359.115(275)	10358.784(257)
$C_e/\text{MHz}$	8845.114(7)	8845.308(114)	8845.014(116)
$\Delta_e/\text{amu Å}^2$	+0.00115(23)	-0.00071(151)	-0.00027(143)
$r_e/\text{Å}$	1.43079 ( $\sigma^D = 1$ ) <sup>a</sup>	1.43079 ( $\sigma^P = 1$ ) <sup>b</sup>	1.43080 ( $\sigma^P = 1$ ) <sup>b</sup>
$\theta_e/^\circ$	119.327 ( $\sigma^D$ )	119.327 ( $\sigma^P = 2$ )	119.329 ( $\sigma^P = 2$ )

<sup>a</sup> $\sigma^D$  denotes the standard deviation obtained by least-squares. <sup>b</sup> $\sigma^P$  denotes the standard deviation obtained using the law of error propagation.

## Results and discussion

As shown in Table 4, the second-order consideration resulted in  $r_c = 1.43080 \text{ \AA}$  ( $\sigma^p=1$ ) and  $\theta_c = 119.329^\circ$  ( $\sigma^p=2$ ). As described above in section (II), the real standard deviations are greater than those given above, probably by a factor of two or three, when we release the constraints of the Fermi and Darling-Dennison resonances in the least-squares calculation. Even so, the results reported in this article provide the most accurate values of the bond distance and bond angle among those reported for triatomic molecules. In a previous article<sup>8</sup> we gave a value  $r_c = 1.4308 \pm 0.0002 \text{ \AA}$ . As a result of the development of spectroscopic techniques in recent years, coupled with elaborate considerations concerning the error limits, the bond distance was refined by one order. The interatomic distances in diatomic molecules are usually determined to six places of decimals.<sup>9</sup> Owing to the fact that polyatomic molecules are subject to various kinds of interactions, the error limits obtained in this article may be the best ones obtained for polyatomic molecules.

In order to see more precisely the effects of the improvements, the molecular structure and inertia defect were also computed, either by neglecting Fermi and Darling-Dennison resonances in the Nielsen approximation,<sup>5</sup> or by neglecting centrifugal distortion effects, i.e. in the Watson approximation.<sup>10</sup> As shown in Table 5, the inertia defect of the  $r_c$ -structure was definitely improved at each step of approximation and finally drop-

ped below its standard deviation, as is required by the theory. This means that the treatment described in this article may well manifest the real situation for  $\text{SO}_2$  molecule. It is true that interactions of even higher order do exist for the vibrational states. For instance, for the  $\text{NO}_2$  molecule, Hoy<sup>11</sup> showed that higher-order Coriolis interactions resulted in significant corrections to the rotational constants. Barbe and coworkers<sup>12</sup> carried out the analysis of the rotational structure of the spectra of ozone by taking Coriolis interactions into account. Considering these factors, a critical examination of Coriolis corrections must be the next problem for the  $\text{SO}_2$  molecule also.

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## Appendix

### *Corrections for transformation of the rotational constants from the Watson to the Nielsen approximation*

As is well known, the rotational constants in the Nielsen approximation are given in terms of  $\tau'$ 's by the relations (A1)–(A3):<sup>13</sup>

$$A^N = A^W - 16 R_6 + (1/2) \tau_{abab} \quad (\text{A1})$$

$$B^N = B^W + 16 R_6(A-C)/(B-C) + (1/2) \tau_{abab} \quad (\text{A2})$$

$$C^N = C^W - 16 R_6(A-B)/(B-C) - (3/4) \tau_{abab} \quad (\text{A3})$$

where

$$R_6 = (1/64)(\tau_{bbbb} + \tau_{cccc} - 2\tau_{bbcc}). \quad (\text{A4})$$

On the other hand, the centrifugal distortion constants,  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$  and  $\delta_K$  have the following relationships (A5–A9) to the  $\tau'$  constants:<sup>10</sup>

$$\Delta_J = -(1/8)(\tau'_{bbbb} + \tau'_{cccc}) \quad (\text{A5})$$

$$\Delta_{JK} = (3/8)(\tau'_{bbbb} + \tau'_{cccc})$$

Table 6. Mean values of corrections to the rotational constants of  $\text{SO}_2$  on going from the Watson to the Nielsen approximation (in MHz).

State	A	B	C
(000)	-0.0252(12)	-0.1352(13)	0.1462(13)
(100)	-0.0291(12)	-0.1382(13)	0.1512(12)
(010)	-0.0299(38)	-0.1500(37)	0.1633(38)
(001)	-0.0210(11)	-0.1303(11)	0.1391(11)
(200)	-0.0330(12)	-0.1412(12)	0.1562(12)
(020)	-0.0349(63)	-0.1644(62)	0.1801(63)
(002)	-0.0169(9)	-0.1253(9)	0.1322(9)
(110)	-0.0338(38)	-0.1529(37)	0.1682(37)
(101)	-0.0249(11)	-0.1333(1)	0.1442(1)
(011)	-0.0257(36)	-0.1452(36)	0.1563(36)
(030)	-0.0401(89)	-0.1785(87)	0.1966(89)

$$-(1/4)(\tau'_{aabb} + \tau'_{bbcc} + \tau'_{aacc}) \quad (\text{A6})$$

$$\Delta_K = -(1/4)(\tau'_{aaaa} + \tau'_{bbbb} + \tau'_{cccc}) + (1/4)(\tau'_{aabb} + \tau'_{bbcc} + \tau'_{aacc}) \quad (\text{A7})$$

$$\delta_j = -(1/16)(\tau'_{bbbb} - \tau'_{cccc}) \quad (\text{A8})$$

$$\delta_K = (1/8)\tau'_{bbbb}(B-A)/(B-C) + (1/8)\tau'_{cccc}(C-A)/(B-C) + (1/8)[\tau'_{aacc} - \tau'_{aabb} + \tau'_{cccc}(2A-B-C)/(B-C)]. \quad (\text{A9})$$

Between  $\tau$  and  $\tau'$  there exist the following relations:

$$\tau'_{aaaa} = \tau_{aaaa} : \tau'_{bbbb} = \tau_{bbbb} : \tau'_{cccc} = \tau_{cccc} \quad (\text{A10})$$

$$\tau'_{bbcc} = \tau_{bbcc} : \tau'_{aacc} = \tau_{aacc} \quad (\text{A11})$$

and

$$\tau'_{aabb} = \tau_{aabb} + 2\tau_{abab}. \quad (\text{A12})$$

Moreover, among  $\tau$  there are three planarity conditions:<sup>14</sup>

$$\tau_{cccc} = \tau_{aaaa}(C/A)^4 + 2\tau_{aabb}(C^2/AB)^2 + \tau_{bbbb}(C/B)^4 \quad (\text{A13})$$

$$\tau_{bbcc} = \tau_{bbbb}(C/B)^2 + \tau_{aabb}(C/A)^2 \quad (\text{A14})$$

and

$$\tau_{aacc} = \tau_{aaaa}(C/A)^2 + \tau_{aabb}(C/B)^2. \quad (\text{A15})$$

Thus, for seven unknown parameters,  $\tau_{aaaa}$ ,  $\tau_{bbbb}$ ,  $\tau_{cccc}$ ,  $\tau_{aabb}$ ,  $\tau_{aacc}$ ,  $\tau_{bbcc}$  and  $\tau_{abab}$ , we have eight relations. We can therefore derive three sets of  $\tau$ 's for the choice of two relations from three planarity conditions. By using these constants the rotational constants in the Nielsen approximation were calculated for each of the three sets of  $\tau$ 's

and their average values were used for the calculations in this survey. Table 6 shows the corrections from the Watson to the Nielsen approximation.

The centrifugal distortion constants for the higher vibrational states used in the above calculations were calculated from those of the (000), (100), (010) and (001) states<sup>1-3</sup> by assuming a linear vibrational dependence. For some of these higher states, the centrifugal distortion constants were already available from infrared measurements. Nevertheless, we used the calculated values for all of them, in order to maintain consistency in the corrections.

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