Accuracy of the equilibrium structure of sulphur dioxide*

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ABSTRACT

The ground state rotational spectra of 12 different isotopologues of sulphur dioxide have been refitted in a consistent way and an accurate experimental cubic force field has been determined. The experimental, semi-experimental and *ab initio* equilibrium structures have been calculated and found in good agreement across themselves. Different approximations limiting the accuracy are discussed. In particular, the influence of centrifugal distortion is analysed. A method is proposed to estimate the higher-order rovibrational corrections (γ -constants). Although an accurate semi-experimental structure was obtained for 19 isotopologues, it was not possible to determine and account for the breakdown of the Born–Oppenheimer approximation. Finally, it was shown that the *ab initio* CCSDTQ level of theory was required to obtain a good agreement with the experimental structure.

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1. Introduction

Assuming that the errors are random, it is possible to use the law of propagation of errors to estimate the accuracy of an equilibrium structure. In many cases, this method concludes that the structure is highly accurate.

As it turns out, however, in the particular case of a structure determination, systematic errors are dominant. First, there is the Born–Oppenheimer approximation. Although it is a very good approximation, it limits the accuracy of the structure of a polyatomic molecule. Then, there is the way the rotation–vibration interaction constants (α - and γ -constants) are obtained. Quite often, they are sensitive to anharmonic resonances and/or Coriolis interactions. The accuracy - or neglect - of higher-order rotation–vibration interaction constants

(γ -constants) also affects the accuracy. Finally, the electronic correction and the centrifugal distortion correction are often neglected although, in some cases, they may have a sizable effect [1–3].

For the sake of completeness, it has also to be remembered that the accuracy of the final structure also used to depend on the accuracy of the Planck constant and of the atomic masses. However, these constants are now highly accurate and the effect of their uncertainty is negligible.

The goal of this paper is to analyse in detail these different approximations, which limit the accuracy of an equilibrium structure in the particular case of sulphur dioxide, SO_2 .

The reasons for this choice are numerous. It is a small triatomic molecule, whose rotational and rovibrational

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spectra have been analysed in great detail [4–6]. The ground state rotational spectra of 19 isotopologues are indeed available.

In the next section, the determination of equilibrium rotational constants is discussed. In the following section, the experimental equilibrium structures of SO₂ are reviewed. Then, an experimental cubic force field of high accuracy is calculated. It allows us to determine an accurate semi-experimental equilibrium structure for 19 isotopologues of sulphur dioxide. After that, a simple method permitting to estimate the contribution of higher-order rovibrational corrections is proposed. The breakdown of the Born–Oppenheimer approximation is investigated. Finally, the *ab initio* Born–Oppenheimer structure is calculated at the coupled-cluster level and compared to the experimental values.

2. Determination of equilibrium rotational constants

2.1. Rovibrational correction [1–3, 7]

The rotational constants X_v for a given vibrational state v of an asymmetric top are given by

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

where $X = A, B$ and C . The summations are over all normal vibrations, each characterised by the quantum number v . The parameters α_i^X and γ_{ij}^X are the vibration–rotation constants and X_e are the equilibrium rotational constants, which are required to determine the equilibrium structure. They may be obtained experimentally by a least-squares fit to Equation (1) using the rotational constants of the ground state and of the excited vibrational states (fundamental, combinations and overtones) as input data. As the excited states are often perturbed by Coriolis interactions and/or anharmonic resonances, it is required to properly treat these interactions. On the other hand, the ground state rotational constants can easily be obtained experimentally, while the α_i^X constants are easily derived from an *ab initio* anharmonic force field (up to cubic terms). Unfortunately, higher-order anharmonic force constants are required for calculating the γ -constants, but there is no theoretical relation so far. For this reason, the effect of the γ -constants on the structure will be analysed below.

2.2. Centrifugal distortion correction [2, 8]

The experimental rotational constants are slightly different from the rigid rotor constants and a small correction due to the centrifugal distortion has to be added. The fitted rotational constants in the asymmetric reduction (A) of Watson [8] (for historical reasons, it is usually preferred for SO₂) have to be corrected using the following relations

$$A = A^A + 2\Delta_J + \frac{1}{2}(\tau_{bbcc} + \tau_{abab}) \quad (2a)$$

$$B = B^A + 2\Delta_J + \Delta_{JK} - 2\delta_J - 2\delta_K + \frac{1}{2}(\tau_{acac} + \tau_{abab}) \quad (2b)$$

$$C = C^A + 2\Delta_J + \Delta_{JK} + 2\delta_J + 2\delta_K + \frac{1}{2}\tau_{aabb} + \frac{1}{4}\tau_{abab} \quad (2c)$$

where A, B and C are the unperturbed rotational constants (after centrifugal distortion correction), whereas A^A, B^A and C^A are the experimental constants resulting from the fit using the A -reduction. The $\tau_{\alpha\beta\gamma\delta}$ constants are the quartic centrifugal distortion constants of Wilson and Howard [9]. They can be approximately determined using the planarity relations [10]. As their vibrational dependence, which may account for more than 10%, is neglected, this correction is not expected to be accurate.

Although it is small, this correction has to be taken into account when very accurate results are desired, and the effect of its neglect will be examined.

Unfortunately, there are additional terms to Equation (2). Watson [11] has shown that there is a mass-dependent contribution to the potential energy. This contribution has the effect of displacing the equilibrium configuration of a particular isotope slightly from the isotopic invariant configuration at the minimum of the potential. This shift of origin will show up in the values of the rotational constants whose equilibrium values are

$$X' = X - \frac{1}{8}(\tau_{xxxx} + \tau_{xxyy} + \tau_{xxzz}) \quad (3)$$

This correction can be important for light molecules but there are still additional terms whose detailed form has not been discussed so far. For this reason, this last correction, Equation (3), is generally neglected. However, its influence will be estimated in the present work.

2.3. Electronic correction [1, 2, 12]

Atomic masses are used to calculate the structure although the centre of mass of the electrons of a bonded atom often does not coincide with the position of its nucleus because the distribution of the electronic clouds

Table 1. Experimental values for the rotation-vibration interaction constants (in MHz) of $^{32}\text{S}^{16}\text{O}_2$.

X	Flaud and Lafferty [17]			Morino and Tanimoto [18]		
	A	B	C	A	B	C
α_1	−33.33(45)	50.023(90)	42.328(91)	−36.41(75)	49.51(12)	41.77(10)
α_2	−1130.36(55)	−2.624(33)	15.685(47)	−1126.68(48)	−2.727(72)	15.864(80)
α_3	616.57(23)	34.954(39)	32.405(46)	613.40(62)	34.11(10)	31.812(81)
γ_{11}	−0.60(22)	0.049(43)	0.104(44)	−2.19(39)	0.126(60)	0.121(51)
γ_{12}	6.86(28)	0.087(55)	0.404(56)	−1.81(80)	−0.049(64)	0.512(57)
γ_{13}	−6.25(40)	0.137(73)	−0.851(80)	−0.33(38)	0.44(55)	−0.588(44)
γ_{22}	24.77(38)	−0.1728(59)	−0.0791(59)	28.83(23)	−0.137(21)	−0.002(35)
γ_{23}	−17.85(40)		−0.422(80)	−18.44(31)	−0.103(40)	−0.485(37)
γ_{33}	3.88(16)	−0.0351(31)	0.0767(31)	1.59(28)	0.148(43)	0.267(36)
γ_{222}	0.571(82)					
$\sum \alpha/2^a$	−273.57(45)	41.177(52)	45.209(56)	−274.84(54)	40.447(86)	44.725(76)
$\sum \gamma/4^a$	−17.85(19)	0.0161(25)	−0.192(33)	1.91(27)	0.105(30)	−0.044(27)
$\gamma_{222}/8$	0.071(10)					
$X_e - X_0^a$	−276.20(49)	41.160(58)	45.401(65)	−276.75(61)	40.342(91)	44.769(81)
X_0	60778.5526(39)	10318.07332(60)	8799.70375(54)			
X_e	60502.21(26)	10359.234(38)	8845.105(40)	60501.77(40)	10358.329(62)	8844.617(47)
	$r_e = 1.430782(15) \text{ \AA}; \angle(\text{OSO}) = 119.3297(30)^\circ$			$r_e = 1.4308302(17) \text{ \AA}; \angle(\text{OSO}) = 119.33042(29)^\circ$		

^aThe uncertainties are calculated using the law of propagation of errors and neglecting the correlations.

around the atoms in a molecule is non-spherical. For this reason, the rotational constants have to be corrected for a small electronic effect. The corrected values of the rotational constants are given by the relation

$$X_{\text{corr}} = \frac{X_{\text{exp}}}{1 + (m/M_p)g_{XX}} \quad (4)$$

where g_{XX} is unitless, m and M_p being the electron and proton masses, respectively.

This last correction, although small, is not negligible in the particular case of SO_2 .

For the $^{32}\text{S}^{16}\text{O}_2$ isotopologue, the experimental g_{XX} values are used: $g_{aa} = -0.6043(3)$; $g_{bb} = -0.11634(12)$; and $g_{cc} = -0.08865(10)$ [13]. It is then possible to calculate them for other isotopologues using the electric dipole moment, $\mu = 1.633 \text{ D}$ [14] and the shift of the centre of mass upon isotopic substitution [15].

3. Experimental equilibrium structures of SO_2

3.1. Isotopologues $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$

The experimental equilibrium structure of $^{32}\text{S}^{16}\text{O}_2$ has been determined many times. Very accurate values were first obtained in 1969 by Saito [16]: $r_e = 1.43076(13) \text{ \AA}$ and $\angle(\text{OSO}) = 119.33(1)^\circ$. More recently, the structure was redetermined using the rotational constants of many more vibrational levels by Flaud and Lafferty [17] and by Morino and Tanimoto [18]. Their results are compared in Table 1. There is a fair agreement between both studies although there are some discrepancies. In particular, the γ -constants are not compatible. The contribution of these γ -terms to the A -rotational constant is about 2 MHz and, comparing the two studies, an uncertainty as large as 1 MHz seems to be realistic. On the other hand,

the contribution of the γ -terms to the B - and C -rotational constants is small.

The ground state inertial defect is $\Delta_0 = 0.1363 \text{ u\AA}^2$ whereas the equilibrium value is $\Delta_e = -0.0003(8) \text{ u\AA}^2$. The uncertainty mainly comes from the rovibrational correction, which means that the equilibrium value Δ_e is not significantly different from zero.

The structure of $^{34}\text{S}^{16}\text{O}_2$ was also accurately determined by Lafferty et al. [19].

The structure of these two isotopologues was recalculated estimating the effect of the different corrections and using more recent ground state rotational constants [20] as well as more accurate g -values [13]. Furthermore, the centrifugal distortion correction was calculated in a more consistent way. The rotational constants and the different corrections are given in Table 2. The centrifugal distortion correction, Equation (2) is quite small but, for the correction to the C -constant, there is a difference of 25% between the experimental value derived from the experimental centrifugal distortion constants and the value calculated from the harmonic force field [21]. The correction due to the mass-dependent contribution to the potential energy, Equation (3), is large for A (1.18 MHz) but almost negligible for B and C .

As there are only two structural parameters and three equilibrium rotational constants, the structure can be obtained in three different ways. The results are given in Table 3. The uncertainties are calculated using the law of propagation of errors, in other words, the systematic errors are not included and the true uncertainty is probably significantly larger.

It seems that the structure derived from the I_a and I_b moments of inertia is the most precise one. However, it does not take into account the large uncertainty of about 1 MHz on the γ -contribution. However, despite

Table 2. Experimental ground state and equilibrium rotational constants of sulphur dioxide with their different corrections.

16.32.16		A / MHz	B / MHz	C / MHz	$\Delta / \text{u}\text{\AA}^2$	Ref.
X_0 exp		60778.54978(29)	10318.073534(51)	8799.703401(45)	0.1363	20
$X_e - X_0$ total ^a	Equation (1)	−276.198(489)	41.160(58)	45.401(65)	−0.0018	17
$\sum \gamma/4$		2.70(19)	0.0161(25)	−0.192(33)		
g -corr.	Equation (4)	19.914	0.656	0.427	0.0012	
cd exp.	Equation (2)	−0.023	−0.136	0.146	−0.0003	
cd calc.		−0.023	−0.128	0.189	−0.0006	
mass dep.	Equation (3)	1.176	−0.045	−0.008	−0.0003	
X_e	Equations (1,2,4)	60522.243	10359.754	8845.677		
$X_e + \text{mass dep.}$	Equations (1,2,3,4)	60523.419	10359.710	8845.670		
16.34.16						
X_0 exp		58991.18295(51)	10318.50993(9)	8761.302481(97)	0.1381	19
$X_e - X_0$ total ^a	Equation (1)	−267.04(254)	40.7265(61)	44.660(94)	−0.0008	
$\sum \gamma/4$		2.275(69)	0.0071(15)	−0.234(31)		
g -corr.	Equation (4)	18.809	0.656	0.424	0.0022	
cd exp.	Equation (2)	−0.022	−0.134	0.144	0.0007	
mass dep.	Equation (3)	1.106	−0.043	−0.007	0.0007	
X_e	Equations (1,2,4)	58742.930	10359.759	8806.531		
$X_e + \text{mass dep.}$	Equations (1,2,3,4)	58744.036	10359.716	8806.524		
16.32.18						
X_0 exp		59101.17304(16)	9724.643842(35)	8331.560892(32)	0.1379	6
$X_e - X_0$ total ^a	Equation (1)	−261.85(16)	37.966(29)	42.124(27)	−0.0011	
$\sum \gamma/4$		3.427(34)	−0.0801(62)	−0.2070(56)		
g -corr.	Equation (4)	19.117	0.580	0.387	0.0020	
cd exp.	Equation (2)	−0.021	−0.123	0.132	0.0004	
mass dep.	Equation (3)	1.111	−0.041	−0.008	0.0004	
X_e	Equations (1,2,4)	58861.839	9762.988	8373.996		
$X_e + \text{mass dep.}$	Equations (1,2,3,4)	58862.950	9762.947	8373.988		

^aIncluding the γ -terms.**Table 3.** Experimental equilibrium structure of sulfur dioxide (distances in Å and angles in degree).

Fit of parameter	I_a, I_b		I_b, I_c		I_c, I_a	
	$\theta = \angle(\text{OSO})$	$r(\text{SO})$	$\angle(\text{OSO})$	$r(\text{SO})$	$\angle(\text{OSO})$	$r(\text{SO})$
³²S¹⁶O₂						
Normal ^a	119.32902(25)	1.4307885(33)	119.3300(16)	1.4307811(96)	119.32884(32)	1.4307848(46)
Without γ ^b	119.33006	1.4307800	119.32605	1.4308090	119.33075	1.4307940
Without distortion ^c	119.32870	1.4307810	119.32496	1.4308090	119.32934	1.4309500
With U ^d	119.32961	1.4307870	119.33062	1.4307800	119.32944	1.4307840
Range	0.00136	0.0000085	0.00566	0.0000290	0.00191	0.0001660
³⁴S¹⁶O₂						
Normal ^a	119.32866(21)	1.4307908(42)	119.3266(13)	1.4308061(96)	119.32903(32)	1.4307987(84)
Without γ ^b	119.32961	1.4307834	119.32203	1.4308388	119.33095	1.4308119
Without distortion ^c	119.32866	1.4307908	119.32656	1.4308061	119.32903	1.4307987
With U ^d	119.32923	1.4307896	119.32714	1.4308049	119.32960	1.4307975
Range	0.00095	0.0000074	0.00511	0.0000338	0.00192	0.0000144
³²S¹⁶O¹⁸O						
Normal ^a	119.32958(10)	1.4307917(16)	119.33311(74)	1.43076594(43)	119.32900(12)	1.43077920(19)
Without γ ^b	119.32792	1.4307979	119.33210	1.43076742	119.32723	1.43078313
Without distortion ^c	119.32928	1.4307849	119.32814	1.43079321	119.32946	1.43078894
Range	0.00166	0.0000130	0.00497	0.0000272	0.00224	0.00000974

^aAll corrections included, except U , Equation (3), see text.^bSee last term of Equation (1).^cSee Equation (2).^dEquation (3).

this uncertainty, the advantage of using I_a and I_b remains. When the mass-dependent contribution to the potential energy (U -term), Equation (3), is considered, the changes are of the same order of magnitude as the precision of the parameters. Obviously, when I_a is not used, the changes are much smaller. As this correction is quite small and as, furthermore, it is not possible to estimate the entire correction, it will be neglected in the following.

When the γ -terms are neglected, the changes are again of the same order of magnitude as the uncertainties, between 3σ (I_a and I_b) and 6σ (I_a and I_c). However, it has to be noted that the α -constants used are the ‘unperturbed’ ones, not those derived from the fundamental vibrations,

$$\alpha_0^X = X_0 - X_1 \quad (5)$$

Table 4. Difference between α_0 and α , $\alpha_{0,v}^X - \alpha_v^X$ with $X = A, B, C$ (in MHz).

v	A	B	C
1	0.89	-0.21	0.02
2	-44.04	0.30	0.17
3	4.29	0.00	0.48

$$\alpha_{0,i} = \alpha_i - 2\gamma_{ii} + (\gamma_{ij} + \gamma_{ik})/2 \text{ with } i, j, k = 1, 2, 3.$$

Table 5. Derivatives $\partial p/\partial X$ (p in Å or degree, X in MHz).

$\partial p/\partial X$	$\partial\theta/\partial X_1$	$\partial\theta/\partial X_2$	$\partial r/\partial X_1$	$\partial r/\partial X_2$
$^{32}\text{S}^{16}\text{O}_2$				
$A = 1; B = 2$	-0.00041	0.00241	0.0000030	0.0000514
$B = 1; C = 2$	0.01649	-0.01932	-0.0000515	0.0001411
$A = 1; C = 2$	-0.00048	0.00331	0.0000015	0.0000706
$^{34}\text{S}^{16}\text{O}_2$				
$A = 1; B = 2$	0.00043	-0.00241	-0.0000031	-0.0000514
$B = 1; C = 2$	-0.01608	0.01892	0.0000484	-0.0001382
$A = 1; C = 2$	0.00050	-0.00334	-0.0000015	-0.0000712
$^{32}\text{S}^{16}\text{O}^{18}\text{O}$				
$A = 1; B = 2$	0.00042	-0.00256	-0.0000031	-0.0000546
$B = 1; C = 2$	-0.01799	0.02098	0.0000580	-0.0001530
$A = 1; C = 2$	0.00050	-0.00348	-0.0000016	-0.0000742

Indeed, the latter α_0 -constants are quite different from the ‘unperturbed’ α -constants because they are significantly altered by the γ -terms, see Table 4. The difference is quite large for the α^A -constants, in particular for the $v = 2$ state. In other words, to determine experimental unperturbed α -constants, it is necessary to take into account the γ -terms. Obviously, this difficulty does not arise when the α -constants are calculated from an anharmonic force field.

Finally, when the centrifugal correction, Equation (2), is neglected, there is a change of the same order of magnitude as the precision of the parameters, except when the pair I_b, I_c is used, where the change is significant. It has also to be noted that it is important to take into account the centrifugal distortion in order to obtain an inertial defect as small as possible, see Table 2. Comparison of the results of Table 3 indicates that the pair I_b and I_c is to be avoided because it gives values, which are less precise and, worse, less accurate. To understand the reasons of this behaviour, the derivatives $\partial p/\partial X$ where p is either $r(\text{SO})$ or $\theta(\text{OSO})$ and $X = A, B, C$ were calculated. They are given in Table 5 and it appears that the derivatives are much larger when the rotational constants B and C are used. Furthermore, as the errors on B and C are of opposite sign, they are additive. For the same reason, with the pair I_b and I_c , the errors are larger when the γ -terms are neglected, although these terms are quite small for B and C .

An experimental equilibrium structure was recently determined for the isotopologue $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ [6]. It is less accurate because it was determined from a small number of experimental data. However, it is also given

in Table 3 and it confirms the conclusions obtained for the other two isotopologues. In summary, it is better to use the pair I_a and I_b to obtain an accurate structure and, taking into account the γ -terms and the centrifugal distortion correction slightly improves the accuracy. Using the results obtained for $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$, it is possible to estimate a robust estimation of the structure, which is the median of the six most accurate values of Table 3 (lines ‘normal’ for the $^{32}\text{SO}_2$ and $^{34}\text{SO}_2$ species). It gives: $r_e(\text{SO}) = 1.4307897(99)$ Å and $\angle(\text{OSO}) = 119.32893(27)^\circ$. The standard deviation is derived from the median absolute value (MAD) of the residuals. The method of the weighted mean, although less robust (because it is more sensitive to errors), gives compatible results: $r_e(\text{SO}) = 1.4307894(22)$ Å and $\angle(\text{OSO}) = 119.32884(13)^\circ$. It is worth noticing that with this latter method, the main difference is that the uncertainties are much smaller. This confirms that the uncertainties used for the weighting are too optimistic.

4. Anharmonic force field of sulphur dioxide

As an anharmonic force field is available for sulphur dioxide, [21] it is possible to determine a semiexperimental structure. However, it is wise to first check the quality of this force field.

There are several experimental determinations of the force field up to quartic terms because the experimental data concerning the α and x (anharmonicity constants) values are abundant for this molecule and because it is one of the few simple systems for which the cubic and most of the quartic potential constants can be determined uniquely, provided all α and x values are known [22]. There are also *ab initio* force fields. In particular, Martin [23] computed an accurate anharmonic force field at the CCSD(T)/cc-pVQZ+1 level of theory. This potential was adjusted by Zúñiga et al. [21], to improve the agreement with observed vibrational energies. Watson [24] found that this latter force field gives good results for the calculation of octic centrifugal distortion constants. It was also found to predict correctly the values of the ground state sextic constants as well as the vibrational dependence of the quartic centrifugal distortion constants [6]. There is also a high-quality *ab initio* potential energy surface from Huang et al. but the force constants are not available [25].

The α -constants calculated from the force field of Zúñiga et al. [21] are compared to the experimental values in Table 6. For the B and C rotational constants of the parent species, the differences are quite small, about 30 kHz (0.08%). On the other hand, the difference for the A -constant is large: about 14 MHz (5%). For $^{34}\text{S}^{16}\text{O}_2$, comparable results are found, except for C where the difference for α_3 is as large as 214 kHz. As the structures

Table 6. Comparison of experimental and calculated α -constants (in MHz).

X	A			B			C		
	Exp.	Calc. ^a	Calc. ^b	Exp.	Calc. ^a	Calc. ^b	Exp.	Calc. ^a	Calc. ^b
$^{32}\text{S}^{16}\text{O}_2^c$									
α_1	−33.33(45)	−25.92	−33.95	50.023(90)	50.412	49.925	42.328(91)	42.717	42.260
α_2	−1130.36(55)	−1109.49	−1130.45	−2.624(33)	−3.549	−2.626	15.685(47)	15.491	15.681
α_3	616.57(23)	610.88	616.27	34.954(39)	35.390	34.970	32.405(46)	32.664	32.427
$X_e - X_0$	−276.198(489)	−262.27	−274.06	41.160(58)	41.127	41.134	45.401(65)	45.436	45.184
$^{34}\text{S}^{16}\text{O}_2^d$									
α_1	−16.94(17)	−8.89	−16.32	49.131(73)	49.681	49.176	41.19(10)	41.705	41.322
α_2	−1095.34(39)	−1074.97	−1095.29	−2.42(71)	−3.337	−2.413	15.83(12)	15.709	15.887
α_3	582.76(24)	577.86	583.03	34.76(61)	35.033	34.618	31.83(85)	32.252	32.024
$X_e - X_0$	−267.04(254)	−253.00	−264.29	40.7265(61)	40.688	40.691	44.660(94)	44.874	44.616
$^{32}\text{S}^{16}\text{O}^{18}\text{O}^e$									
α_1	−43.88(12)	−36.86	−44.65	46.454(25)	46.819	46.393	35.692(24)	39.926	39.518
α_2	−1066.14(27)	−1049.28	−1069.08	−2.699(45)	−3.438	−2.596	14.156(40)	13.962	14.148
α_3	593.17(11)	588.12	593.11	32.016(26)	32.670	32.277	33.985(26)	30.299	30.071
$X_e - X_0$	−258.43(15)	−249.01	−260.31	37.886(28)	38.026	38.037	41.917(26)	42.094	41.868

^aForce field of Zúñiga et al. [21].^bForce field of this work.^cRef [17].^dRef [19].^eRef. [6].**Table 7.** Quadratic and cubic force field of sulphur dioxide.

Parameter	Unit	.Ref. [26]	Ref. [18].-	.Ref. [21]	.Ref. [27]	This work
f_{rr}	$\text{aJ } \text{\AA}^{-2}$	10.410	10.362(9)	10.29387	10.390(34)	10.29403(34)
$f_{rr'}$	$\text{aJ } \text{\AA}^{-2}$	0.120	0.016(9)	−0.01858	0.067(31)	−0.01707(34)
$f_{r\alpha}$	$\text{aJ } \text{\AA}^{-1}$	0.563	0.185(10)	0.24806	0.423(64)	0.24042(54)
$f_{\alpha\alpha}$	aJ	1.640	1.652(2)	1.65668	1.6516(52)	1.65667(13)
f_{rrr}	$\text{aJ } \text{\AA}^{-3}$	−69.8	−68.80(12)	−70.68798	−72.66(43)	−70.415(30)
$f_{rrr'}$	$\text{aJ } \text{\AA}^{-3}$	0.5	−0.69(7)	−0.75170	−1.81(25)	−0.537(19)
$f_{rr\alpha}$	$\text{aJ } \text{\AA}^{-2}$	1.1	−1.01(12)	−0.94749	−2.90(61)	−0.8375(52)
$f_{rr'\alpha}$	$\text{aJ } \text{\AA}^{-2}$	1.9	−0.75(2)	−0.68010	−1.488(95)	−0.6954(52)
$f_{r\alpha\alpha}$	$\text{aJ } \text{\AA}^{-1}$	0.1	−1.95(4)	−1.9226	−3.248(84)	−1.8690(69)
$f_{\alpha\alpha\alpha}$	aJ	−2.3	−2.13(1)	−2.09574	−2.688(98)	−2.1959(19)

derived from the B and C semiexperimental rotational constants of $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$ give almost identical structures, it might be due to an experimental problem.

Furthermore, there is obviously a problem with the α^A -constants, see Table 6, for instance, the experimental value of α_1^A is −33.33 MHz whereas the computed value from the force field of Zúñiga is only −25.92 MHz. As the α -constants only depend on the quadratic and cubic force constants, it is possible to try to find the origin of the problem.

It is now possible to determine an accurate experimental quadratic force field. There are indeed enough accurate data for the vibrational frequencies of $^{32}\text{S}^{16}\text{O}_2$ [17] and $^{34}\text{S}^{16}\text{O}_2$ [19] to derive harmonic frequencies for all vibrations. Furthermore, as the quartic force field of Zúñiga et al. [21] seems to be reliable, it is also feasible to derive accurate values for the equilibrium values of the quartic centrifugal distortion constants [6]. In other words, there are 16 experimental data to determine four quadratic force constants. The experimental data are listed in Tables S1 and S2 of the Supplementary

Material and the fitted force constants are compared in Table 7 to the previous determinations. The agreement is extremely good and the discrepancies observed for the α^A -constants cannot be explained by inaccuracy of the quadratic force constants.

The next step is to refine the cubic force constants (six parameters) using the accurate experimental α -constants of $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$ (18 values). The least-squares system of normal equations is extremely well-conditioned and very accurate corrections are obtained. The improved values of the cubic constants are also given in Table 7. The improvement is best visible by comparing the mean of absolute values of the residuals: for the α^A -constants, it decreases from 1.87 MHz to 0.05 MHz, for the α^B -constants, the improvement is as expected smaller, from 97 kHz to 9 kHz, and, finally, for the α^C -constants, the change is still smaller from 53 kHz to 13 kHz. This confirms that there is a problem with the α^C -constants, particularly for the $^{34}\text{S}^{16}\text{O}_2$ isotopologue.

Inspection of Table 7 confirms the difficulty to obtain accurate off-diagonal constants for the force field.

5. Semiexperimental equilibrium structures of SO₂

The modulus operandi is almost the same as for the experimental structure but with two differences. The most important one is that the α -constants, Equation (1), are not determined experimentally but are calculated from a cubic force field. Furthermore, the γ -constants are neglected.

The main advantage of this method is that only ground state rotational constants are required, provided an anharmonic force field is available. This is quite important because it is easy to determine accurate ground state rotational constants and, indeed, the ground state rotational spectra of 19 isotopologues of sulphur dioxide have been analysed. However, in order to have comparable results, it is necessary to use rotational constants of the same quality for all isotopologues.

5.1. Ground state rotational constants

Accurate ground state rotational constants are available for ³²S¹⁶O₂ [20], ³³S¹⁶O₂, ³²S¹⁶O¹⁷O [28], ³⁴S¹⁶O₂ [19], ³²S¹⁶O¹⁸O and ³²S¹⁸O₂ [6]. For the other species, Van Riet [29] has assigned many transitions. For a complete list of references, see [4] where a full set of rotational constants is also listed. However, the results of the fits are of very different quality. For this reason, most of the spectra were reanalysed using the mixed estimation method [30, 31]. In this method, auxiliary information is added to the data matrix for the least-squares fits. This auxiliary information, called predicate observations by us are approximate values of the quartic and sextic centrifugal distortion constants. For symmetric substitutions of atoms in SO₂ C_{2v} molecules, centrifugal distortion constants P and P' of the ground vibrational states of the main and substituted species can be estimated using the following relation [32]

$$P'_{ij} = \left(\frac{A[\text{S}^{18}\text{O}_2]}{A[\text{S}^{16}\text{O}_2]} \right)^i \left(\frac{C[\text{S}^{18}\text{O}_2]}{C[\text{S}^{16}\text{O}_2]} \right)^j P_{ij} \quad (6)$$

where i is the power of J_z^2 in the Hamiltonian and j the value of $(m - 2i)/2$, m being the total power of the corresponding term.

For the isotopologues of C_s symmetry, it was assumed that the variations upon isotopic substitution are additive. For instance,

$$\begin{aligned} P_{ij}[\text{S}^{33}\text{S}^{16}\text{O}^{18}\text{O}] \\ = P_{ij}[\text{S}^{32}\text{S}^{16}\text{O}^{18}\text{O}] + P_{ij}[\text{S}^{33}\text{S}^{16}\text{O}_2] - P_{ij}[\text{S}^{32}\text{S}^{16}\text{O}_2] \end{aligned} \quad (7)$$

This approximation gives satisfactory results in most cases because the rotation of the principal axes upon isotopic substitution is quite small.

The choice of the associated uncertainty for the weighting of the predicates is important: 10% of the value of the parameter gave satisfactory results. Furthermore, an extensive residual analysis [30] was performed to check the weighting and to identify possible misassignments. In most cases, the sextic constants Φ_{JK} and ϕ_{JK} have a negligible contribution to the frequencies. For this reason, they were kept fixed at the predicted values. However, as these predicted values are derived from experimental values, which are rather inaccurate, they have to be considered as fitting parameter without physical value. The rotational parameters are listed in Table S3 of the Supplementary Material.

5.2. Structure from the improved force field

First, it is useful to look at the I_b^{SE} moments of inertia of the C_{2v} isotopologues because it allows us to check the accuracy of the force field. Indeed,

$$I_b^e = 2m(\text{O})r^2 \sin^2 \frac{\theta}{2} \quad (8)$$

Thus, dividing I_b^{SE} by the mass of oxygen permits to obtain $r \sin(\theta/2)$, which is isotopically invariant. The results are shown in Table S4 of the Supplementary Material. The median value is $r \sin(\theta/2) = 1.23489232(11)$ Å. It is extremely accurate and the invariance is well verified. As expected, the largest deviations are found for the isotopologues with nuclear quadrupole hyperfine structure because their ground state rotational constants are one order of magnitude less accurate. The range at 10^{-5} Å is 10 times larger than the standard deviation but, if the isotopologues with nuclear quadrupole hyperfine structure (NQHFS) are eliminated (³³S and ¹⁷O), it decreases to 2×10^{-6} Å.

In principle, it is also possible to use the I_a^{SE} moments of inertia to derive $r \cos(\theta/2)$ which should be invariant upon isotopic substitution but the situation is more complicated because the γ -terms are not negligible. This point will be discussed in Section 6.

The structure was determined from the moments of inertia I_a and I_b in the same way as in Section 3 using the improved force field of Section 4. The result for each isotopologue is given in Table S5 of the Supplementary Material and their median values in Table 8. The standard deviation is calculated from the MAD. It is a robust estimator but it does not take into account the systematic errors, which are probably not negligible. However, it is possible to estimate their effect. From the comparison with the experimental values, it is possible to assign

Table 8. Semiexperimental structure (SE) of sulphur dioxide (bond length in Å and angle in degrees).

Force field	Used data	$\theta_e = \angle(\text{OSO})$			$r_e(\text{SO})$		
		Median	mean	exp – se	median	mean	exp – se
Exp.		119.32893(27)			1.4307897(99)		
This work	l_a, l_b	119.329872(81)	119.329665	0.00094	1.4307858(15)	1.4307879	–0.0000039
This work + scaling ^a	l_a, l_b	119.328783(55)	119.328740	–0.00015	1.43079396(93)	1.4307947	0.0000043
This work + scaling ^a	l_b, l_c	119.331264(23)	119.330900	0.00233	1.4307767(14)	1.4307777	–0.0000130
Ref[21]. + scaling ^a	l_a, l_b	119.328811(40)	119.328771	–0.00012	1.4307943(10)	1.4307950	0.0000047

^aThe scaling was used to estimate the contribution of the γ -terms, see text

Table 9. Experimental and calculated rovibrational corrections $A_e - A_0$ (MHz) for several isotopologues of sulphur dioxide.

Isotopologue	16.32.16	16.34.16	16.32.18	18.34.18 ^a
From the force field ^b	–262.3	–253.0	–249.0	–227.6
Force field ^b + scaling ^c	–276.2	–266.4	–262.2	–239.7
Improved force field ^d	–274.6	–264.3	–260.3	–237.9
Experimental value ^e	–276.2	–267.0	–261.9	
From r_e^f	–276.5	–266.4	–262.8	–239.7
From r_e^{SEg}	–277.1	–267.0	–263.4	–240.3

^aHeaviest isotopologue.

^bRef. (21).

^cScaling factor = 276.198/262.265 = 1.053.

^dThis work, see text.

^eSee Table 2.

^fDerived from the ground state rotational constant and the experimental equilibrium structure.

^gDerived from the ground state rotational constant and the semiexperimental equilibrium structure.

an error of about 2 MHz to $A_e - A_0$ (mainly due to the neglect of the γ -terms) and less than 0.1 MHz for $B_e - B_0$, see Tables 6 and 9. It gives an error of 0.0009° for the angle and 0.000008 Å for the bond length. It is almost one order of magnitude larger than the standard deviation derived from the MAD. Another way to estimate the accuracy is to make a comparison with the experimental structure. For the angle, the difference is $\theta^{\text{SE}} - \theta^{\text{EXP}} = 0.0009^\circ$ and, for the bond length, it is $r^{\text{SE}} - r^{\text{EXP}} = -0.000004$ Å. These values are in agreement with the preceding estimation.

The main weak point of this method is that the γ -terms are neglected whereas they are not negligible for the A -constant. However, this problem can be remedied by scaling the force field value $\Delta A = A_e - A_0$. As the range of ΔA is not large, about 35 MHz, it is possible to scale the force field values using the experimental value of the parent species, which is probably the most accurate one. In other words, the force field values of ΔA are multiplied by 276.198/274.06 (experimental value/computed value). The result for each isotopologue is also given in Table S5 of the Supplementary Material and their median values in Table 8. The standard deviation of the parameters is indeed slightly smaller and the comparison with the experimental values better: $\theta^{\text{SE}} - \theta^{\text{EXP}} = -0.00015^\circ$ for $\angle(\text{OSO})$ and, for the bond length, it is $r^{\text{SE}} - r^{\text{EXP}} = 0.000004$ Å for the bond length.

5.3. Structure from the force field of Zúñiga et al. [21]

The case of sulphur dioxide is extremely favourable because there is enough accurate experimental data permitting to calculate a reliable force field up to cubic terms. For this reason, it is interesting to investigate the possibility to determine a semiexperimental structure from the existing force field of Zúñiga et al. [21].

The main difficulty is the large systematic error for $A_e - A_0$, which makes difficult to determine an accurate structure using the A and B rotational constants because it would induce a systematic error of about 0.006° on the $\angle(\text{OSO})$ angle and 4×10^{-4} Å on the SO bond length. Using instead B and C reduces significantly the systematic error: less than 0.00014° for the angle and less than 4×10^{-5} Å for the bond length. Compared to the uncertainty of the experimental structure, 0.00027° for the angle and 10^{-5} Å for the bond length, using B and C seems acceptable although not perfect. The detailed results are given in Table S5 of the Supplementary Material and their median values in Table 8. The standard deviation of the parameters is quite small but the comparison with the experimental values less favourable: $\theta^{\text{SE}} - \theta^{\text{EXP}} = 0.00233^\circ$ and, for the bond length, it is $r^{\text{SE}} - r^{\text{EXP}} = -0.000013$ Å. For the $\angle(\text{OSO})$ angle, it is almost ten times the standard deviation of the experimental value.

Fortunately, it is still possible to calculate the semiexperimental structure using the A and B rotational constants. The force field value of $\Delta A = A_e - A_0$ is only 5% of the experimental value (in absolute value). As the range of ΔA is not large, it is possible to scale the force field values as done in Section 5.2. In other words, the force field values of ΔA are multiplied by $(\sum \alpha/2)_{\text{exp}}/(\sum \alpha/2)_{\text{forcefield}} = 276.198/262.265$. To check that this method does not induce errors larger than one MHz, the scaled values are compared to the experimental values and to the values derived from the best experimental structure in Table 9. The agreement is indeed satisfactory and allows us to determine a structure, which is likely to be accurate as it is confirmed by the results. The detailed results are given in Table S5 of the Supplementary Material and their median values in Table

8. The standard deviation of the parameters is quite small and, more interestingly, the comparison with the experimental values quite favourable: $\theta^{\text{SE}} - \theta^{\text{EXP}} = -0.00012^\circ$ and, for the bond length, it is $r^{\text{SE}} - r^{\text{EXP}} = -0.000005 \text{ \AA}$. In other words, the accuracy is comparable to that found with the improved force field based on a scaling of ΔA , although the method is much simpler.

6. Estimation of the γ -parameters

It is tempting to try to obtain $r \cos(\theta/2)$ from I_a^{SE} because

$$I_a^e = 2 \frac{m(\text{O})m(\text{S})}{M} r^2 \cos^2 \frac{\theta}{2} \quad (9)$$

where M is the total mass of the molecule. Unfortunately, the result is not constant as it should be but increases with the mass of the molecule. This is mainly due to the neglect of the γ -constants in the calculation of I_a^{SE} .

The higher-order rovibrational constants, γ , Equation (1), are not negligible for molecules with large rotational constants as SO_2 . However, their determination requires the rotational constants of many vibrationally excited states, most of them being perturbed. As a consequence, these γ -constants are often inaccurate, one of the few exceptions being $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$. It is their contribution to the moment of inertia, I_e , which is interesting. It may be written

$$I_e(a, g) = I_e(a) - \delta(g) \quad (10)$$

where $I_e(\alpha, \gamma)$ is the equilibrium moment of inertia calculated taking into account the α - and γ -constants whereas $I_e(\alpha)$ is the equilibrium moment of inertia calculated by only taking into account the α -constants, and

$$\delta(\gamma) = \frac{h}{8\pi^2} \frac{\sum \gamma/4}{B_e^2(\alpha, \gamma)} \quad (11)$$

For S^{16}O_2 it gives (in $\text{u}\text{\AA}^2$) 0.000373(27) for the ^{32}S species and 0.000333(1) for the ^{34}S species. These values are close. Furthermore, it has to be noted that all the γ -constants are assumed to be free of perturbation, which is unlikely. Actually, for a diatomic molecule, using the expression of the Dunham constant $Y_{21} = \gamma$ [33], it is possible to show that $\delta(\gamma)$ is invariant upon isotopic substitution. We may assume that it remains a valid approximation for the C_{2v} isotopologues of SO_2 for which there is no rotation of the principal axis system upon isotopic substitution. This assumption may be checked by calculating $I_a(r)$ from the best equilibrium structure and comparing it to the semi-experimental value I_a^{SE} . The results are shown in Table S6 of the Supplementary Material, where the less accurate species with quadrupole hyperfine structure have been dropped.

Taking into account the uncertainties, it may be concluded that the $\delta(\gamma)$ value may be assumed to be constant upon isotopic substitution with a mean value of $\delta(\gamma) = 0.000402(13) \text{ u}\text{\AA}^2$. This value is slightly larger than the experimental values but the standard deviation does not take into account the systematic errors.

There is a simpler way to determine $\delta(\gamma)$ by using the least-squares method where the input data are the I_a^{SE} and the parameters to be determined are $\delta(\gamma)$ and $r \cos(\theta/2)$. The results are: $\delta(\gamma) = 0.00066(18) \text{ u}\text{\AA}^2$ and $r \cos(\theta/2) = 0.7226533(76) \text{ \AA}$. These results are not expected to be very accurate because the number of data is quite small, six. However, taking into account the small number of degrees of freedom, the value of $\delta(\gamma)$ is compatible with the previous determinations. Furthermore, using the value of $r \sin(\theta/2)$ determined in Section 5.2, it allows to obtain an equilibrium structure in good agreement with the previous determinations: $r = 1.4307994(55) \text{ \AA}$ and $\theta = 119.32805(28)^\circ$.

It is tempting to try to calculate the structure by using the differences of moments of inertia. The differences eliminate the contribution of $\delta(\gamma)$ as well as the systematic errors. However, this method has to be used with caution because the difference of two close values is an unstable operation. This is one of the main shortcomings of the substitution method [34, 35].

7. *Ab initio* equilibrium structure

There was some debate concerning the structure of SO_2 when compared to O_3 , the latter molecule having a rather large biradical character. This was solved by Takeshita et al. [36] who showed that SO_2 has a closed shell nature with a double-bonded structure. Thus, the structure optimisation of SO_2 should be easier than that of O_3 .

The coupled-cluster theory including single and double excitations (CCSD) [37] augmented with a perturbational estimate of the effects of connected triple excitations, CCSD(T) [38], with a basis set of quadruple zeta quality (cc-pwCVQZ or aug-cc-pwCVQZ for polar bonds) [39] is known to give satisfactory results. For a collection of molecules containing second-row atoms, it was found that the bond lengths are too large by 0.00024 $\text{\AA}$ (mean value) with a standard deviation of only 0.00097 $\text{\AA}$ [40]. This good result is mainly due to a compensation of errors because the introduction of connected quadruples (CCSDTQ) increases the bond length by 0.001–0.002 $\text{\AA}$ whereas the basis set extension from quadruple zeta to sextuple zeta shortens it by about the same amount. Thus, although the convergence of the geometry is not fully achieved at the quadruple zeta level, using a larger basis set should not improve much the result.

Table 10. Born-Oppenheimer equilibrium structure of SO₂ (distances in Å and angles in degree).

Method	Basis set	$r(\text{SO})$	$\theta = \angle(\text{OSO})$
$r_e(\text{exp})^a$		1.4307897(99)	119.32893(27)
$r_e(\text{SE})^b$		1.43079396(93)	119.328783(55)
CCSD(T)_AE	aug-cc-pwCVTZ	1.43613993	119.35052
CCSD(T)_AE	aug-cc-pwCVQZ	1.43109531	119.38922
CCSD(T)_AE	aug-cc-pwCV5Z	1.42957226	119.36741
CCSD(T)_AE	aug-cc-pwCV6Z ^a	1.42786	119.440
CCSD(T)_AE	aug-cc-pwCV ∞ Z	1.42797	119.344
CCSD(T)-F12_AE ^c	cc-pVQZ-F12	1.42977	119.3618
CCSD(T)-F12_FC	aug-cc-pV5Z-F12 ^d	1.42958	119.3567
CCSDTQ	^e	1.4305	119.40
MRCI-F12 ^d	aug-cc-pV5Z	1.42964	119.3968
Extrapolation ^f		1.43087716	119.32333

^aCorrection V5Z $\rightarrow$ V6Z calculated with the MP2/aug-cc-pVnZ level of theory.^bSee Table S5.^cThe CCSD(T)-F12b approach has been used with a scaling of the triples.^dAfter correction for the core correlation, see Table S8.^eSee Table S7.^fSee text.

The structure was optimised at the CCSD(T) level of theory by means of the Molpro programme [41, 42], all electrons being correlated (AE) with the aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets. The results are given in Table 10. Although the convergence is not completely achieved at the aug-cc-pwCVQZ level, the bond length is only 0.0003 Å too large, and, as anticipated, the results are more accurate with this later basis set than with the larger aug-cc-pwCV5Z for which the bond length is 0.0012 Å too short. Actually, the basis set convergence is not yet achieved at the aug-cc-pwCV5Z level. Furthermore, the rather large value of the coupled-cluster T_1 diagnostic [43] at 0.022 (CCSD/cc-pVTZ value) indicates that the possible existence of some non-dynamical correlation explaining the slow convergence of the CCSD(T) method, this implies that it would be necessary to go beyond CCSD(T).

First, the CCSD(T) structure was estimated at infinite basis size by extrapolating the aug-cc-pwCVQZ and aug-cc-pwCV5Z results with the following empirical equation [44]

$$\Delta r(\text{CBS}) = \frac{n^3 r(n) - (n-1)^3 r(n-1)}{n^3 - (n-1)^3} - r(n-1) \quad (11)$$

where n indicates the cardinal number of the larger basis set. This extrapolation formula is known to have an accuracy of about 0.001 Å when only first-row atoms are involved, at least for covalent bonds. In the case of SO₂, the accuracy of the extrapolation could be worse. To confirm the correct order of magnitude of this correction, the structure was also optimised at the CCSD(T) level of theory with the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The correction (aug-cc-pV5Z $\rightarrow$ aug-cc-pV6Z) is

$\Delta r = -0.00171$ Å and $\Delta\theta = +0.073^\circ$. These corrections confirm the validity of the extrapolation.

One difficulty with the CCSD(T) method is its slow convergence. To obviate it, we exploited the much faster convergence of the explicitly correlated CCSD(T)-F12 method [45], used with the cc-pVnZ-F12 [46] and cc-pCVnZ-F12 [47] basis sets series, specifically optimised for the F12 approaches. Indeed, when going from cc-pVQZ-F12 to cc-pV5Z-F12, the decrease in bond length and in bond angle is of 0.0002 Å and 0.004°, respectively, with the CCSD(T)-F12 method, whereas it is of 0.0015 Å and 0.022°, respectively, with the standard CCSD(T) method. However, it does not solve the problem of the non-dynamical correlation, the bond length being too short after core correction, see Table S7 of the Supplementary Material. We first compared the standard aug-cc-p-VnZ and cc-pVnZ-F12 basis sets, see Table S7 of the Supplementary Material. It indicates that, at the V5Z level, the difference is almost negligible: +0.00018 Å for the bond length and -0.0054° for the bond angle. However, it is known that combining F12 methods with basis sets not specifically optimised for them may lead to erratic convergence [48]. For this reason, we also used the recently developed aug-cc-pVnZ-F12 basis sets of Sylvetsky et al. [49], which includes d to h diffuse functions in addition to cc-pVnZ-F12. We adopted in our calculations their recommendations for the values of the geminal exponent and for the choice of the resolution of identity (RI) complementary auxiliary basis set. The results are also given in Table S7 of the Supplementary Material. They show that the additional diffuse functions do not act significantly on the geometry. Including the core correction, the (aug)-cc-pV5Z-F12 and cc-pCVQZ-F12 results are almost identical, taking into account the fact that the extension of the basis set from VQZ to V5Z leads to a tiny shortening of 0.00021 Å for the bond and of 0.0039° for the angle. These results are better than with the CCSD(T)_AE/aug-cc-pwCVnZ values, which are too small for $n \geq 4$, see Table 10. However, the bond length is still slightly too short by 0.0002 Å compared to the experimental values.

It remains the problem of the non-dynamical correlation. To investigate it, the structure was first optimised with the CFOUR programme [50] at the CCSD, CCSD(T), CCSDT and CCSDTQ [51] levels of theory. Because the CCSDTQ calculation is extremely time consuming, small basis sets were used: cc-pVDZ, DZP, TZP [52], and def-SVP [53]. It is fortunately known that the small correction CCSD(T) $\rightarrow$ CCSDTQ can be estimated with such small basis sets [54].

These calculations confirm the lengthening of the bond length of about 0.0025 Å and the shortening of the bond angle of about 0.09° when going from CCSD(T) to

CCSDTQ. The detailed results are given in Table S8 of the Supplementary Material and the final results in Table 10.

To do away with this difficulty, instead of using the CCSDTQ method, we carried out calculations with the multireference configuration interaction method (MRCI) [55] and, more specifically, the MRCI-F12 method [56, 57] implemented in Molpro. In these calculations, the contribution of unlinked clusters was taken into account by means of the Davidson correction for relaxed reference [58]. The detailed results are also given in Table S7 of the Supplementary Material and the final result in Table 10. As shown in Table 10, the MRCI value is in perfect agreement with the CCSD(T)-F12 results, indicating that the non-dynamical correlation effects are probably not important.

As a further check, it might be interesting to try the extrapolation of the computed *ab initio* rotational constants to infinite basis set limit in order to reproduce the experimental GS rotational constants. This method should minimise the effects of the slow convergence. This modus operandi was developed by Kummli *et al.* [59]. The structure is optimised at the triple (aug-cc-pwCVTZ) and quadruple (aug-cc-pwCVQZ) zeta levels with the CCSD(T) method and the parameters are extrapolated so that the derived rotational constants are equal to the semiexperimental rotational constants. However, this method does not give satisfactory results because the distance between the aug-cc-pwCVTZ and aug-cc-pwCVQZ results is large (0.005 Å for r) and the relationship between the rotational constants and the geometrical parameters is obviously not linear. In the present case, it is better to use the moments of inertia and $d_a = [r \cos(\theta/2)]^2$ and $d_b = [r \sin(\theta/2)]^2$ as parameters. The moments of inertia may be written

$$I_g(x) = a_g + b_g \times d_g(x)$$

with $g = a, b$ and $x = \text{wCVTZ, wCVQZ or experimental}$. a_g and b_g are determined using $x = \text{wCVTZ}$ and wCVQZ , then, $d_g(\text{experimental})$ is obtained using $I_g(\text{experimental})$. This method gives good results, see Table 10 and is not sensitive to the accuracy of the rovibrational corrections ΔA and ΔB with $\partial r / \partial \Delta A = -0.000003 \text{ Å MHz}^{-1}$, $\partial r / \partial \Delta B = -0.000005 \text{ Å MHz}^{-1}$, $\partial \theta / \partial \Delta A = 0.00041 \text{ degree MHz}^{-1}$, and $\partial \theta / \partial \Delta B = -0.00024 \text{ degree MHz}^{-1}$. Comparing the experimental rovibrational corrections with the *ab initio* values computed by Martin [23], we may assume an error of 4%, which implies an uncertainty of $4 \cdot 10^{-5} \text{ Å}$ for r and of 0.005 degree for θ . Comparison with the semiexperimental structure shows that the extrapolated values are slightly more accurate than the CCSD(T)_AE/cc-pwCV n Z ones. However, this method cannot be applied to larger molecules. Interestingly, when compared to

either the experimental, or semiexperimental, or extrapolated values, the CCSD(T)_AE/cc-pwCVQZ results are accurate and there is not much improvement by using either the CCSD(T)-F12 or the MRCI methods.

8. Conclusion

The equilibrium structure of sulphur dioxide has been determined using either the experimental or the semiexperimental methods. The effect of different approximations on the accuracy has been tested and, at the end, an accurate equilibrium structure has been obtained independently for nineteen isotopologues. In particular, a simple method permitting to estimate the contribution of the γ -constants is proposed.

As the final accuracy is high, about 10^{-5} Å , it is possible to verify whether the Born–Oppenheimer breakdown (BOB) may be observed. The Born–Oppenheimer (BO) approximation has been studied in great detail for diatomic molecules. A typical example is CO. The CO bond length calculated from the equilibrium rotational constant of $^{12}\text{C}^{16}\text{O}$ is 1.128336 Å, but Watson [60] has shown that the BO length is 1.128243 Å, that is, a difference of 10^{-4} Å . There is no quantitative theory for polyatomic molecules. However, very accurate analyses indicate that the BO breakdown is also visible in linear triatomic molecules as CO_2 [61]. The possibility of the BO breakdown has also been tested in the case of $\text{HC} \equiv \text{CH}$ [62, 63]. To point out a BOB, it is enough to check whether the geometry varies with the mass of the molecule. No such effect was observed and it can thus be concluded that the BOB is smaller than 10^{-4} Å .

Supplementary Material

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