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***Ab initio* quantum chemical study of the molecular and spectroscopic (infrared and Raman) properties of sulfur dioxide: Comparison with ozone**

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Using *ab initio* SCF, singles and doubles configuration interaction (CI-SD), and coupled pair functional (CPF) techniques with basis sets of triple zeta plus two polarization functions quality, the following properties have been computed for sulfur dioxide at its equilibrium geometry: dipole and quadrupole moments, electric field gradients at the nuclei, static and frequency dependent dipole polarizability (at $\lambda = 5154 \text{ \AA}$ and $\lambda = 6328 \text{ \AA}$), dipole and polarizability derivatives, infrared absorption intensities, and Raman scattering activities. The properties, when calculated at the correlated level of theory have been evaluated by the energy derivative (ED) as well as the expectation value (EV) formalism. The results of the CPF(ED) calculations are in good agreement with the available experimental data and on the basis of additional two-configurational MCSCF studies the use of single reference CI-SD and CPF wave functions is judged to be justified. The analogous calculations on ozone serve to highlight the considerable differences between the two molecules, inasmuch as due to the considerably larger degree of near-degeneracy in O_3 , properties that involve mixing of the lowest 1B_2 excited state with the 1A_1 ground state are predicted poorly at the SCF level as well as at the single reference CI-SD and CPF levels of theory.

I. INTRODUCTION

Ozone is one of the most important species in our atmosphere and, as such, it has been studied extensively by both experimental and theoretical techniques, although both approaches are subject to difficulties. Owing to its reactive and unstable nature certain bulk properties of ozone are difficult to measure experimentally, thus spectroscopy has been the main tool used in its study. *Ab initio* quantum chemical studies on the other hand are hampered by the well known problem of O_3 being poorly described by Hartree-Fock SCF theory. Consequently a correlated study of the 1A_1 ground state of ozone should ideally start with a multiconfigurational SCF (MCSCF) reference containing at least the two configurations¹⁻⁴:

$$1a_1^2 \cdots 6a_1^2 1b_2^2 \cdots 4b_2^2 1b_1^2 1a_2^2$$

and

$$1a_1^2 \cdots 6a_1^2 1b_2^2 \cdots 4b_2^2 1b_1^2 2b_1^2,$$

since the $1a_2$ and $2b_1$ π molecular orbitals are near-degenerate.

Replacing the central oxygen atom in ozone by sulfur results in another well known and important molecule: sulfur dioxide. In contrast with ozone, SO_2 is an air pollutant and as it is a consistent by-product of many industrial processes, it is also an important molecule to understand well. As sulfur dioxide is a quite stable molecule, experimental physico-chemical studies on it are inherently easier than for O_3 and indeed there is a wealth of experimental information available for SO_2 . Whether it is also a simpler molecule to study at the theoretical level has not been explicitly addressed. With some exceptions,⁵⁻⁷ most *ab initio* quantum chemical studies on SO_2 have been carried out at the SCF level, on the ground as well as several of the excited states,^{8,9} concentrating on the simpler electronic properties,⁹⁻¹³ equilibrium geometries^{7,9,11,12} as well as attempting to under-

stand in terms of simple valence concepts the electronic structure of SO_2 , in particular the importance of *d*-orbital participation in the bonding.¹⁴⁻¹⁸

The primary aim of this work was to carry out reasonably good quality *ab initio* correlated calculations on the ground state of the sulfur dioxide molecule and calculated a range of one-electron properties, namely the dipole and quadrupole moments, electric field gradients at the nuclei, dipole polarizabilities, as well as the dipole moment and polarizability derivatives which yield estimates of the infrared absorption intensities and Raman scattering activities. Where possible, the calculated properties are compared with the corresponding experimental values. The secondary aim of this study is to determine whether the SO_2 molecule is adequately described by a single configuration SCF wave function and, by extension, by a configuration interaction (CI) or coupled pair functional (CPF) wave function which is constructed as a single reference plus all single and double excitations from it. Thus some of the crucial SCF calculations are repeated using small MCSCF wave functions. Finally, the SO_2 results are compared with the analogous results for O_3 , in an attempt to highlight the similarities and differences between the two molecules.

II. THEORY AND COMPUTATIONAL METHODS

The majority of the calculations in this work were carried out using wave functions generated by the Hartree-Fock SCF, single reference singles and doubles configuration interaction (CI-SD) and coupled pair functional (CPF) methods. The CPF method, recently developed by Ahlrichs *et al.*¹⁹⁻²¹ is a size consistent modification of the CI-SD approach and is closely related to the CEPA1 scheme of Meyer²² and Ahlrichs.^{23,24} Consequently, it allows for the approximate treatment of those higher order excitations that can be developed as unlinked clusters of the doubles.^{25,26} An

alternative, simpler way of accounting for such higher excitations is to use Davidson's correction.²⁷

The validity of the single reference results was checked when necessary, by performing two-configuration MCSCF calculations; the latter were carried out using the complete active space SCF (CASSCF) method of Roos *et al.*^{28–30}

At the correlated level the electronic properties were calculated both as expectation values (EV) and as energy derivatives (ED), i.e., by calculating the gradient $dE(\lambda V)/d\lambda$, given the perturbed Hamiltonian,

$$\hat{H}(\lambda V) = \hat{H}_0 + \lambda \hat{V}, \quad (1)$$

where \hat{V} is the operator representing a component of the given property. As discussed in considerable detail elsewhere,^{31–37} wave functions that are not fully optimized, such as CI-SD, do not satisfy the Hellmann–Feynman theorem, consequently

$$\frac{dE(\lambda V)}{d\lambda} \neq \langle \Psi_0 | \hat{V} | \Psi_0 \rangle, \quad (2)$$

where Ψ_0 is an eigenfunction of H_0 , i.e., there are two distinct ways of calculating one-electron properties. In such a case the ED formalism is expected to be the more accurate as it accounts for the first-order effects of the orbital relaxation in a limited CI wave function, in other words, the variational flexibility of the wave function is exploited to a larger degree in the ED approach than is implicit in the EV method.^{37–39} The difference between the EV and ED predictions of a given property is the non-Hellmann–Feynman term (NHFT).

In the CEPA schemes there is no rigorous expectation value formalism, thus an advantage of the CPF method over CEPA is that a one-particle density matrix γ can be defined, namely through the requirement that

$$\left(\frac{\partial E(\lambda V)}{\partial \lambda} \right)_{\lambda=0} = \left(\frac{\partial}{\partial \lambda} E_0 + \frac{\partial}{\partial \lambda} F_c[\Psi_c, H(\lambda V)] \right)_{\lambda=0} = \text{tr } \gamma \mathbf{V}, \quad (3)$$

where $F_c[\Psi_c, H(\lambda V)]$ represents the CPF energy functional.¹⁹ As the derivative $\partial F_c/\partial \lambda$ in Eq. (3) does not account for variations in the SCF MOs under the perturbation λV , using γ , as defined above, to calculate properties, is formally equivalent to the EV approach.

In a previous paper³⁷ we developed a convenient formalism for the analytical calculation of EDs within the framework of CI-SD wave functions. This method exploits the \mathbf{Z} vector approach of Handy and Schaefer,⁴⁰ and can readily be extended to allow complete orbital optimization of a CI-SD wave function, yielding a CI-SD/MCSCF wave function which obeys the Hellmann–Feynman theorem. Thus, where possible, the energy derivatives have been calculated by the above analytical approach. Extension of this method to cover the case of the simplest coupled cluster wave functions (CEPA0) is trivial⁴¹; not so however for the other CEPA type wave functions. An implicit advantage of the energy functional formulation is, however, that the evaluation of analytical first derivatives of the energy is fairly straightforward in principle as the derivatives of the CI coefficients are

not required. Pulay has, with this aim in mind, proposed two CEPA schemes which being formulated as energy functionals allows readily the calculations of the analytical derivatives,⁴² while more recently, the gradient of the CPF energy has been derived by Rice, Lee, and Handy.⁴³ A new CPF approach, the averaged coupled pair functional (ACPF) method,⁴⁴ developed mainly for multireference work, is in fact simpler than the original CPF, hence energy gradients for it at the single reference level are no more difficult than for CEPA0.⁴¹

According to previous experience with the CPF method^{45,46} in calculating electric field gradients for a range of small molecules, the EV and ED predictions differ more than at the CI level. To some extent this must be due to the fact that the correlation corrections to a given property at the CPF level are significantly larger than with CI and the magnitude of the NHFT mirrors the increased contribution of the correlating term to the total wave function. In addition, it should be kept in mind that CPF and CEPA wave functions are not variational and include the unlinked cluster effect in approximate ways; when these approximations break down, i.e., the coefficients of the double excitations are overestimated, a large NHFT results. This follows from the fact that as the NHFT can be written in the form of a Brillouin matrix element,³³ its magnitude directly depends on the coefficients of the double (and single) excitations. The breakdown of the CEPA approximations has been most graphically demonstrated previously in the calculation of potential energy curves: when a bond is stretched by about 50%, as a result of the increased near degeneracy the CEPA curves turn downwards, i.e., become completely unphysical.⁴⁷ As the possibility of such problems exists in the present work, the CPF results are closely scrutinized and, where necessary, will be critically discussed.

The calculations reported in this paper were carried out using several different program packages on two different computers. The main body of the calculations was performed on the CYBER205 computer of CSIRO Australia, utilizing the CYBER205 version of the COLUMBUS programs.^{19–21,48} The CASSCF, CI/MCSCF, and certain other SCF and CI calculations were carried out using the MOLECULE programs^{28,30,49–52} on our microVAXII computer, while the frequency dependent polarizability calculations were performed using CADPAC,⁵³ also on the microVAXII. As the current version of the COLUMBUS codes does not contain analytical gradient codes at the correlated level, the properties, when defined as EDs were calculated by the finite field method. Depending on the type of perturbation, the field values (λ) chosen were in the range of 0.001–0.01 a.u. All the dipole moment and polarizability derivatives quoted in this paper were then obtained by numerical differentiation of the calculated dipole moment and polarizability functions at a range of distorted geometries that were chosen as symmetry adapted atomic Cartesian distortions,⁵⁴ their magnitude being in the range of 0.02–0.05 bohr.

Three basis sets of similar quality have been used. The bulk of the calculations were carried out using basis A that utilizes the Chandler–McLean (12,9) sulfur basis⁵⁵ contracted to [6,5], according to the scheme (631111,42111),

and extended by three sets of $3d$ polarization functions ($\zeta = 0.6, 0.2, 0.07$), while the oxygen basis is Dunning's [5,3] contraction of the (9,5) primitive set,⁵⁶ plus two sets of $3d$ functions ($\zeta = 1.0, 0.2$). The second basis set B is the sulfur (11,7) Huzinaga basis,⁵⁷ contracted (531111,31111)⁵⁸ to [6,5] and extended by three sets of $3d$ functions ($\zeta = 0.6, 0.2, 0.07$), and the oxygen (9,5) basis contracted to [4,3], as recommended by Dunning,⁵⁶ to which two sets of $3d$ functions ($\zeta = 0.8, 0.2$) were added. The third basis C used only in the polarizability calculations for SO_2 is basis B extended by an extra set of diffuse s and p functions on both S and O [$\zeta_{s,p}(\text{S}) = 0.05, \zeta_{s,p}(\text{O}) = 0.08$]. Basis C was used in an earlier SCF study¹⁰ of the polarizability tensor of SO_2 ; in this work it is also used to calculate the polarizability derivatives. It should also be noted that the COLUMBUS programs utilize only the five pure $3d$ orbitals, while MOLECULE and CADPAC use six Cartesian d functions which then result in one extra $3s$ orbital per $3d$ set in comparison with the COLUMBUS bases. Differences that arise as a result of this variation in the basis set will be noted, where appropriate. In the correlated calculations the sulfur $1s, 2s, 2p$ and the oxygen $1s$ atomic orbitals are kept frozen to substitutions.

The equilibrium geometries in these calculations were taken from experiment, thus for SO_2 ⁵⁹ the SO bond length is 1.432 Å and the bond angle is 119.5°, while in O_3 ⁶⁰ the bond length is 1.278 Å and the bond angle is 116.8°. The coordinate system used in these calculations is shown in Fig. 1.

The infrared (IR) intensities and Raman scattering activities have been calculated in the double harmonic approximation.⁶¹⁻⁶⁴ The expression for the IR intensities is thus given as³⁶

$$I_i = 974.8644 \sum_{\mu} \left[\frac{\partial \mu}{\partial Q_i} \right]^2, \quad (4)$$

where the derivative of the dipole moment μ with respect to the set of normal coordinates $\{Q_i\}$ is given in $e u^{-1/2}$, the intensity of the i th band is then in km mol^{-1} and the summation is over all degenerate modes. The Raman scattering activities for plane polarized light are defined as^{63,64}

$$A_i = g_i [45(\alpha'_i)^2 + 7(\gamma'_i)^2], \quad (5)$$

where α'_i is the derivative of the mean polarizability $\bar{\alpha}$ with

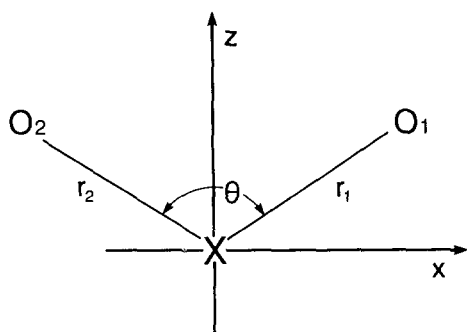


FIG. 1. The coordinate system used in the SO_2 and O_3 calculations (X = S or O).

respect to Q_i and $(\gamma'_i)^2$ is the square of the analogous polarizability derivative anisotropy. The above expression, originally derived by Placzek,⁶⁵ applies to "off-resonance" Raman bands and the scattering activity A_i is directly proportional to the Raman scattering cross section. Another quantity of interest is the degree of depolarization ρ_i of the Raman scattered light, given as

$$\rho_i = 3(\gamma'_i)^2 / [45(\alpha'_i)^2 + 4(\gamma'_i)^2]. \quad (6)$$

As in previous studies of ours, the derivatives of the dipole moment and polarizability tensor were first calculated with respect to the full set of atomic Cartesian displacements.^{36,54} From this data, given the normal coordinates, also expressed in terms of the atomic Cartesian coordinates, the derivatives with respect to the normal coordinates and hence the intensities are readily calculated. The normal coordinates of SO_2 and O_3 used here were generated from the experimental force constants,^{66,67} as described in full elsewhere.⁵⁴

III. RESULTS AND DISCUSSION

A. Equilibrium energies, dipole moments, quadrupole moments, and electric field gradients

In Tables I and II the equilibrium energies and the calculated properties obtained at the various levels of theory, for SO_2 and O_3 , are summarized. In the case of SO_2 we note a near-monotonic progression in the calculated properties from SCF to CI(EV) to CPF(EV), with the unlinked cluster correction, viz. CPF-CI difference, being very large, in contrast with the total energy where the major part of the correlation energy is recovered at the CI-SD level. The differences in the calculated properties when obtained by the EV and ED formalisms are quite small in the case of CI, but considerably more pronounced at the CPF level. Similar trends have been noted previously by Cummins *et al.*⁴⁵ in a study of electric field gradients of small molecules. As argued in the previous section as well as elsewhere,^{45,46,68} the CPF(ED) predictions are believed to be the most accurate and reliable and, in general, we find that for SO_2 agreement with the available experimental estimates is best when this method is used, although the CI(ED) estimates with Davidson's correction are also quite good. Thus, the CPF(ED) dipole and quadrupole moments as well as the electric field gradients at the sulfur atom are in quite good agreement with experiment, considering the experimental uncertainties in the definition of the origin for the quadrupole moment tensor and in the magnitude of the quadrupole moment of the ^{33}S nucleus. No experimental data seems to be available for the ^{17}O quadrupole coupling constant, thus the accuracy of the field gradients at the oxygen atom cannot be ascertained, although they appear to be fairly stable with respect to level of theory. For these reasons, as well as due to the relatively high cost of the (correlated) ED calculations, only expectation value estimates were obtained for this property. The inclusion of excitations from the sulfur $2s$ and $2p$ orbitals in the CI and CPF wave functions results in a considerable drop in the total energy ($E_{\text{CI}} = -547.836\,291\,E_h$, $E_{\text{CPF}} = -547.851\,354\,E_h$), but has negligible effect on the calculated properties, changing the latter by $\leq 1\%$. Compar-

TABLE I. Sulfur dioxide: total energies (E), dipole moment (μ_α), quadrupole moment ($\theta_{\alpha\beta}$, at center of mass), electric field gradients ($V_{\alpha\alpha}$), and asymmetry parameters (η) at the sulfur^a and oxygen^b nuclei calculated using the SCF, CI, CPF, and CASSCF methods with basis A. All quantities given in atomic units.

Property	SCF	CI(EV)	CPF(EV)	CI(ED)	CI(ED)/Dav. ^c	CPF(ED)	CASSCF-2	Experiment
E	-547.248 465	-547.742 395	-547.816 329		-547.803 142		-547.277 532	
μ_z	-0.772 9	-0.686 1	-0.545 4	-0.6908	-0.655 3	-0.6307	-0.653 1	-0.6400 ^d
θ_{xx}	-4.360 4	-3.950 2	-3.263 4	-3.9414	-3.763 1	-3.6523	-3.707 5	-3.94 ^e
θ_{yy}	3.378 5	3.138 4	2.665 9	3.0962	2.974 1	2.9056	2.964 7	2.97 ^e
θ_{zz}	0.981 9	0.811 8	0.597 5	0.8452	0.789 0	0.7467	0.742 8	0.97 ^e
V_{xx} (S)	0.043 5	0.096 4	0.276 4	0.1398	0.185 8	0.2029	0.516 1	0.11 ^f
V_{yy} (S)	2.047 4	1.767 7	1.163 2	1.6212	1.444 2	1.3559	1.050 7	1.57 ^f
V_{zz} (S)	-2.090 9	-1.864 1	-1.439 6	-1.7610	-1.630 0	-1.5588	-1.566 8	-1.68 \pm 0.01 ^f
η	0.958 4	0.896 6	0.616 0	0.8412	0.772 0	0.7397	0.341 1	0.87 ^f
V_{xx}^p (O)	0.609 1	0.562 0	0.381 0				0.522 5	
V_{yy}^p (O)	0.877 9	0.793 7	0.801 3				1.038 2	
V_{zz}^p (O)	-1.487 0	-1.355 7	-1.182 3				-1.560 7	
η	0.180 8	0.170 9	0.355 5				0.330 4	

^a In molecular frame (Fig. 1).

^b In principal axis system.

^c CI(ED) with Davidson's correction.

^d Reference 69.

^e Reference 70.

^f From quadrupole couple constants in Ref. 71 using $Q(^{35}\text{S}) = -0.065$ b.

ing the two-configuration MCSCF results with those calculated using SCF and single reference correlated wave functions, we note that the changes from SCF are substantial and generally in the "right" direction, i.e., resulting in better agreement with experiment and/or the CI and CPF estimates. An exception is the field gradient on the sulfur atom where the MCSCF predictions for the xx and yy components, and hence the asymmetry parameter, are in substantial disagreement with all the other theoretical and experimental values. Nevertheless, on the basis of these results it seems safe to conclude that the single reference CPF wave function is capable of yielding accurate values for the electronic properties of SO_2 .

Comparing the ozone results (Table II) with SO_2 , the trends in the calculated quantities are quite similar when going from SCF to the CPF(ED) levels of theory but the O_3 properties calculated using the two-configuration MCSCF wave function differ markedly from the SCF estimates, much more so than in SO_2 . The erratic behavior of the O_3 dipole moment with respect to changes in the orbital spaces in post-SCF calculations has been well documented by Adler-Golden *et al.*,⁴ who also found, in agreement with this

work, that a single reference CI-SD wave function yields quite a good dipole moment. Going beyond the CI-SD treatment, we find that the CPF(ED) method slightly overshoots the correlation correction to the dipole moment, although agreement with experiment is comparable with that for SO_2 . The variation in the quadrupole moment components from SCF to CPF(ED) levels of theory are also comparable with those in SO_2 , and the agreement with experiment at the CPF(ED) level is quite similar in both molecules.

From the above results it appears that the near-degeneracy problems that require a multireference treatment are more severe in ozone than in sulfur dioxide. This conclusion is corroborated by the fact that in SO_2 the gain in energy is $0.0269 E_h$ when the SCF wave function is made two-configuration MCSCF (calculated with basis set A, including the $3s$ components of the Cartesian $3d$ sets), while in O_3 the corresponding energy gain is $0.0947 E_h$. Also, coefficients of the two configurations in the MCSCF wave functions are 0.978 and -0.207 in SO_2 , to be compared with 0.885 and -0.466 , respectively, in O_3 . Consequently, it is not surprising that O_3 is much more of a problem case than SO_2 .

TABLE II. Ozone: total energies (E), dipole moment (μ_α), and quadrupole moment ($\theta_{\alpha\beta}$, at center of mass) calculated using the SCF, CI, CPF, and CASSCF methods with basis A. All quantities given in atomic units.

Property	SCF	CI(EV)	CPF(EV)	CI(ED)	CI(ED)/Dav. ^a	CPF(ED)	CASSCF-2	Experiment
E	-224.319 467	-224.889 378	-224.992 391		-224.966 559		-224.417 444	
μ_z	-0.293 2	-0.254 5	-0.116 9	-0.2414	-0.213 5	-0.1902	-0.056 2	-0.210 ^b
θ_{xx}	-1.358 0	-1.267 2	-0.906 9	-1.3572	-1.179 9	-1.1198	-0.765 1	-1.041 ^b
θ_{yy}	1.144 6	1.229 9	1.259 7	1.2656	1.290 5	1.3022	1.314 8	1.561 ^b
θ_{zz}	0.213 4	0.037 3	-0.352 8	0.0916	-0.110 6	-0.1824	-0.549 7	-0.520 ^b

^a CI(ED) with Davidson's correction.

^b Reference 72.

B. Dipole polarizabilities, polarizability derivatives, and Raman scattering activities

The components of the dipole–dipole polarizability tensors calculated for SO₂ and O₃ are listed in Tables III and IV. In the case of SO₂ the correlation corrections to the polarizability are small, ~6% on average, and positive, comparable to what is found in most small molecules where the single reference based wave functions are believed to be adequate.^{77–80} The CI(EV) and CI(ED) values are very close, as found also in the case of first-order properties, and we note that the CPF(ED) results are closely paralleled by the Davidson corrected CI(ED) values, although the latter have not been included in Table III. Basis A, however, that was used in these correlated calculations lacks diffuse *s* and *p* orbitals which could be of some importance in the calculation of the polarizabilities. Thus, the static polarizability was recalculated at the SCF level using both bases B and C. As noted in the previous section, the 3*d* sets in these two bases contain six Cartesian *d* orbitals, but basis C also has the diffuse *s,p* set on all the atoms. The differences between the calculated SCF polarizabilities with bases A and B are quite small but there is a considerable increase in all components when going to basis C; the changes are comparable to the calculated correlation corrections. As the experimental measurements of the polarizability tensor had been carried out at the optical frequencies of 5154 and 6328 Å, further calculations were performed in order to estimate the frequency dependence of the polarizability. These calculations,

TABLE III. Sulfur dioxide: components of the static dipole polarizability tensor ($\alpha_{\alpha\beta}$) calculated using the SCF, CI, CPF, and CASSCF methods (with basis set A unless otherwise indicated) and estimates of the dynamic polarizability tensor at wavelengths of 5154 and 6328 Å. All quantities given in atomic units.

Calculation	α_{xx}	α_{yy}	α_{zz}
SCF	30.33	17.69	19.70
CI(EV)	31.37	17.92	20.47
CI(ED)	31.47	17.96	20.60
CPF(ED)	32.43	18.36	21.52
SCF(basis A') ^a	30.80	18.08	20.16
CASSCF-2(basis A') ^a	31.72	18.48	20.90
SCF(basis C) ^b	31.72	18.54	20.71
SCF(basis B)	30.69	17.70	19.72
SCF(basis B) $\lambda = 5154$ Å	31.98	18.39	20.11
SCF(basis B) $\lambda = 6328$ Å	31.52	18.12	19.98
CPF(ED)/corr; $\lambda = 5154$ Å ^c	35.11	19.90	22.92
CPF(ED)/corr; $\lambda = 6328$ Å ^c	34.65	19.63	22.79
Experiment $\lambda = 5154$ Å	35.881 ^d	20.292 ^d	23.693 ^d
Experiment $\lambda = 6328$ Å ^f	36.6 ± 1.8	19.2 ± 1.2	23.0 ± 0.7

^a Basis A' is the same as basis A but includes 3*s* contributions from Cartesian 3*d* sets.

^b Reference 9.

^c CPF(ED) results corrected for basis set effects and frequency dependence.

^d Reference 73.

^e Reference 74.

^f Reference 75.

TABLE IV. Ozone: components of the static dipole polarizability tensor ($\alpha_{\alpha\beta}$) calculated using the SCF, CI, CPF, and CASSCF methods with basis A. All quantities given in atomic units.

Calculation	α_{xx}	α_{yy}	α_{zz}
SCF	36.99	10.23	11.74
CI(EV)	34.01	10.35	11.92
CI(ED)	30.98	10.29	12.01
CPF(ED)	40.38	10.65	12.50
CASSCF-2	23.71	10.29	11.94
Experiment	31.0 ^a	12.1 ^a	13.5 ^a

^a Reference 72.

as indicated in the previous section, were carried out at the SCF level, using the time-dependent Hartree–Fock formalism,^{81–83} with basis B. As the results show, the polarizability increases with increasing frequency, resulting in improved agreement with experiment. However, to obtain a more realistic theoretical estimate of the frequency dependent polarizability we corrected our best correlated, viz., CPF(ED) results, for basis set incompleteness and frequency dependence by adding on the difference in the SCF polarizabilities calculated using basis C and A and the differences between the frequency dependent and static polarizabilities. Such a correction procedure for correlation effects, while not rigorous, has been found to be reasonably accurate as there is some evidence that the correlation corrections to a given property converge faster with respect to a finite basis than the SCF values.^{45,46,68,84} Our corrected estimate of the polarizability tensor at $\lambda = 5154$ Å is in fact in very good agreement with the experimental values, the deviation being ~2% in the mean polarizability. We note however, that as the experimental polarizability components at $\lambda = 5154$ Å in fact represent one of two sets of values that are consistent with the actual experimentally measured quantities, namely the mean polarizability,⁷⁴ Raleigh depolarization ratio,⁷⁴ and Raman contours of the pure rotational spectrum of SO₂,⁷³ the current theoretical estimates quite unambiguously confirm the “assignment” of the experimental polarizability components. At the wavelength $\lambda = 6328$ Å our theoretical polarizability tensor is in similarly close agreement with the experimentally determined tensor.⁷⁵ Finally, comparing the SCF and two-configuration MCSCF polarizabilities (calculated using basis A, containing the 3*s* contribution from the 3*d* sets), it is evident that the differences are fairly small, indicating that the initial single configuration wave function is quite accurate in predicting the polarizability, i.e., there appear to be no major near-degeneracy problems. The situation is very different for the ozone molecule (Table IV), where the *xx* component of the polarizability shows large variations with the type of calculation. The first thing to note is that the SCF and two-configuration MCSCF predictions are very different for α_{xx} , but agree closely in the case of α_{yy} and α_{zz} . The massive discrepancy in the case of α_{xx} can be attributed to the fact that in ozone there is a low lying electronic state of *B*₂ symmetry which would make a large contribution to α_{xx} , as the latter can formally be written as a sum over states, viz.,

$$\alpha_{xx} = -2 \sum_{i \neq 0} |\langle \Psi_0 | \hat{\mu}_x | \Psi_i \rangle|^2 / (E_0 - E_i), \quad (7)$$

where $\{\Psi_i\}_{i \neq 0}$ represents singlet states with B_2 symmetry. The CASSCF calculations with just the $1a_2$ and $2b_1$ orbitals active predict the lowest lying 1B_2 state to be $0.245 E_h$ above the 1A_1 ground state, while at the SCF level this energy difference is just $0.150 E_h$, hence the large difference between the SCF and MCSCF values α_{xx} . In contrast to this, in SO_2 the analogous CASSCF and SCF estimates of the above energy difference are 0.284 and $0.257 E_h$, i.e., SCF is describing it quite well, hence its reliability in predicting α_{xx} . Thus in O_3 α_{xx} is overestimated by the SCF method; this is contrary to the usual observation that correlation effects increase the polarizability.^{77–79} Given that the SCF treatment is seriously in error it is not surprising that the correlated estimates based on single-reference wave functions show very large fluctuations. In such situations the (variational) CI method using the ED formalism is expected to be the most reliable, as there are strong indications that the approximations inherent in the CPF method are breaking down. On the other hand, the correlated estimates of the other polarizability components, α_{yy} and α_{zz} , are expected to be reasonably accurate, the main source of possible improvements being the basis set. Unfortunately, owing to the molecule's reactive nature, the only experimental estimates of the polarizability tensor of O_3 are from rotational quadratic Stark effect measurements,^{72,76} where accuracy is inherently limited. The experimental values for α_{xx} , α_{yy} , and α_{zz} quoted in Table IV were determined by Mack and Muentner,⁷² who combined their measured anisotropy values with a mean polarizability of $18.9 a_0^3$ that had been quoted in a theoretical paper by Nagarajan.⁸⁵ Due to inconsistencies in the literature references of Nagarajan the origin of the above mean polarizability could not be traced, hence it is not possible to quote experimental errors in the polarizability tensor, although, on the basis of the results of Meerts *et al.*,⁷⁶ a figure of 10%–20% seems reasonable. Assuming such error estimates, the current CI values, EV as well as ED, are indeed consistent with experiment.

Given that in SO_2 the static polarizability is reasonably well described at the SCF level, the calculations were extended to the prediction of the polarizability derivatives with respect to nuclear distortions from which the Raman scattering activities can be derived using the double harmonic approximation.^{61,63,64} The Cartesian polarizability derivatives (CPD) were calculated by numerical differentiation of the polarizability tensor that had been computed using the coupled perturbed Hartree–Fock (CPHF) method^{50,86,87} at distorted geometries, corresponding to displacements of $\pm 0.05 a_0$ in the x and z directions (Fig. 1). Using the symmetry properties of the CPD tensor in a molecule with C_{2v} symmetry the CPDs for O_2 can be obtained from those of O_1 , while the sulfur CPDs can be obtained via the null condition,^{54,88}

$$\sum_n \alpha_{\alpha\beta,\gamma(n)} = 0, \quad (8)$$

where

$$\alpha_{\alpha\beta,\gamma(n)} = \frac{\partial \alpha_{\alpha\beta}}{\partial \gamma(n)}, \quad (9)$$

and the index n labels the atoms. The calculated CPDs that contribute to Raman scattering activities are listed in Table V, together with the derivatives with respect to the usual symmetry coordinates, defined with respect to the set of space fixed axes so that they satisfy the Eckart–Sayvetz conditions.^{89,90} Given that the normal coordinates fairly closely resemble the symmetry coordinates it is immediately obvious that the most intense Raman band in SO_2 will correspond to the symmetric stretch, due to a large extent to the very large derivative of α_{xx} , which is also the largest component of the polarizability tensor.

The average polarizability derivatives and squared anisotropy derivatives with respect to the normal coordinates are given in Table VI, together with the resulting Raman scattering activities and depolarization ratios which are also compared with experiment. Unfortunately, it is only the symmetric stretch for which good quality Raman scattering cross-section data exist. For this mode the predicted scattering activity of $24.35 \times 10^{-8} \text{ cm}^4 \text{ g}^{-1}$ is in good agreement with the average of the available data $26.4 \times 10^{-8} \text{ cm}^4 \text{ g}^{-1}$, based on a tabulation of Schrötter and Klöckner,⁶⁴ considering that the scatter in the data is almost 10%. Utilizing the limited experimental data for the intensity of the bending mode results in scattering activities^{91,92} which differ by an order of magnitude, but bracket the calculated value. The calculations also predict the antisymmetric stretch to have a considerably large Raman activity, which is in reasonable agreement with the experimental estimate, based on relative intensity data.⁹¹ The calculated depolarization ratios are also consistent with experiment.⁹¹

As we could not, as yet, calculate the full polarizability tensor of ozone with sufficient accuracy, we did not attempt the calculation of the Raman intensities for it.

TABLE V. Sulfur dioxide: nonzero Cartesian polarizability derivatives ($\alpha_{\alpha\beta,\gamma}$) of O_1 (Fig. 1) and derivatives with respect to symmetry coordinates^a ($\partial \alpha_{\alpha\beta} / \partial S_i$) for ${}^{32}\text{S}^{16}\text{O}_2$ calculated at the SCF level with basis C. All quantities given in atomic units.

$\alpha_{xx,x}$	14.630
$\alpha_{yy,x}$	2.245
$\alpha_{zz,x}$	2.483
$\alpha_{xz,x}$	3.576
$\alpha_{xx,z}$	6.030
$\alpha_{yy,z}$	0.581
$\alpha_{zz,z}$	3.398
$\alpha_{xz,z}$	4.437
$\partial \alpha_{xx} / \partial S_1$	22.168
$\partial \alpha_{yy} / \partial S_1$	3.157
$\partial \alpha_{zz} / \partial S_1$	5.454
$\partial \alpha_{xx} / \partial S_2$	2.162
$\partial \alpha_{yy} / \partial S_2$	0.629
$\partial \alpha_{zz} / \partial S_2$	−1.685
$\partial \alpha_{xz} / \partial S_3$	6.813

^aSymmetry coordinates: $S_1 = 2^{-1/2}(\delta r_1 + \delta r_2)$, $S_2 = r_c \delta \theta$, $S_3 = 2^{-1/2}(\delta r_1 - \delta r_2)$.

TABLE VI. Sulfur dioxide ($^{32}\text{S}^{16}\text{O}_2$): harmonic frequencies ω_i (cm^{-1}), mean polarizability derivatives α'_i ($a_0^3 E_h^{-1} u^{-1/2}$), squared polarizability derivative anisotropies $(\gamma'_i)^2$ ($a_0^6 e^4 E_h^{-2} u^{-1}$), depolarization ratios ρ_i , and Raman scattering activities A_i ($10^{-8} \text{ cm}^{-1} \text{ g}^{-1}$) for plane polarized light, calculated at the SCF level with basis C.

Mode and symmetry	Calculation					Experiment	
	ω_i	α'_i	$(\gamma'_i)^2$	ρ_i	A_i	ρ_i	A_i
$\nu_1(A_1)$	1166.6	-2.8250	22.36	0.150	24.35	0.16 ^a	26.4 ± 2.4^b
$\nu_2(A_1)$	526.3	-0.0980	2.03	0.712	0.69	0.68 ^a	$0.2^c, 1.9^d$
$\nu_3(B_2)$	1381.7	0.0	15.21	0.750	5.03	0.75 ^a	3.2^d

^a Reference 91.

^b Based on scattering cross-section data quoted in Ref. 64.

^c Reference 92.

^d Relative intensities from Ref. 91 scaled by 26.4.

C. Dipole moment derivatives in infrared absorption intensities

An SCF study of the dipole derivatives of SO_2 was carried out a few years ago using basis C, from which it was concluded that electron correlation was likely to have a large effect on these properties and hence on the IR intensities.⁹³ Thus a primary aim of this study has been to carry out accurate correlated calculations on SO_2 with a view of studying in some detail the behavior of the dipole moment derivatives at various levels of theory. As in our polarizability studies, we first generated the Cartesian dipole moment derivative (CDMD) tensor ($\mu_{\alpha,\beta(n)}$) for the O_1 atom (Fig. 1). In analogy with the CPD tensor, the CDMDs for the other atoms can be generated by the use of symmetry and the null condition^{36,54}

$$\sum_n \mu_{\alpha,\beta(n)} = 0, \quad (10)$$

where n labels the atoms and

$$\mu_{\alpha,\beta(n)} = \frac{\partial \mu_\alpha}{\partial \beta(n)}. \quad (11)$$

In the literature CDMD tensor are also referred to as atomic polar tensors.⁹⁴⁻⁹⁶ Tables VII and VIII contain the calculated CDMD's for SO_2 and O_3 . The trends in the dipole derivatives of SO_2 are very similar to those already noted for other properties such as the dipole moment itself: as more correlation is allowed for, the CDMDs decrease in magnitude. Again, the CI(EV) and CI(ED) predictions are very close. As before, the CPF(ED) results are regarded as the most accurate and the agreement between them and experiment⁹⁶ is quite good. However, we find that, in our coordinate system (Fig. 1), the signs of $\partial \mu_z / \partial S_1$ and $\partial \mu_z / \partial S_3$ are negative, but $\partial \mu_z / \partial S_2$ is positive. This is in disagreement with the choice of signs by Kim and King⁹⁶ who, on the basis of STO-4G SCF calculations, concluded that $\partial \mu_z / \partial S_2$ was also negative. Thus, when comparing with experiment (Table VII), we quote the set of CDMDs of Kim and King⁹⁶ that is

TABLE VII. Sulfur dioxide: nonzero Cartesian dipole moment derivatives ($\mu_{\alpha,\beta}$) of O_1 (Fig. 1), derivatives with respect to symmetry coordinates^a ($\partial \mu_\alpha / \partial S_i$) and infrared absorption intensities^b (I_i) calculated at the SCF, CI, and CPF levels of theory with basis A. All derivatives given in atomic units, IR intensities given in km mol^{-1} .

	SCF	CI(EV)	CI(ED)	CPF(ED)	Experiment	
$\mu_{x,x}$	-1.105	-0.986	-0.956	-0.863	-0.854 ± 0.004^c	
$\mu_{z,x}$	-0.065	-0.042	-0.040	-0.001	-0.041 ± 0.006^c	
$\mu_{x,z}$	-0.479	-0.428	-0.411	-0.370	-0.362 ± 0.003^c	
$\mu_{z,z}$	-0.634	-0.551	-0.545	-0.467	-0.433 ± 0.003^c	
$\partial \mu_z / \partial S_1$	-0.5311	-0.4439	-0.437	-0.3339	-0.3586^d	-0.414^e
$\partial \mu_z / \partial S_2$	0.5149	0.4548	0.4506	0.4029	0.353^d	0.354^e
$\partial \mu_x / \partial S_3$	-1.7416	-1.5542	-1.5053	-1.3585	-1.3426^d	-1.301^e
$I_1(A_1)$	44.7	32.3	31.4	20.4	20.6 ± 0.7^c	25 ± 1^f
$I_2(A_1)$	53.9	42.0	41.2	32.8	25.3 ± 0.3^c	25.2 ± 0.5^f
$I_3(B_2)$	322.9	257.2	241.2	196.5	192 ± 2^c	189 ± 5^f

^a Symmetry coordinates defined in Table V.

^b IR intensities for $^{32}\text{S}^{16}\text{O}_2$; normal coordinates generated from experimental force constants.

^c Reference 96.

^d Calculated from CDMDs in Ref. 96.

^e Reference 97.

^f Reference 98.

TABLE VIII. Ozone: Dipole moment derivatives with respect to symmetry coordinates^a ($\partial\mu_\alpha/\partial S_i$) and infrared absorption intensities^b (I_i) calculated at the SCF, CI, and CPF levels of theory with basis A. All derivatives given in atomic units, IR intensities given in km mol⁻¹.

	SCF	CI(EV)	CI(ED)	CPF(ED)	Experiment
$\partial\mu_z/\partial S_1$	0.1888	0.1639	0.1954	0.2447	0.224 ^c
$\partial\mu_z/\partial S_2$	0.1666	0.1570	0.1590	0.0795	0.121 ^c
$\partial\mu_x/\partial S_3$	-2.5656	-2.0136	-0.9021	-3.7969	-0.766 ^c
I_1	0.008	0.002	0.05	2.3	1.1 ± 0.3^d
I_2	6.8	5.9	6.3	2.2	4.3 ± 0.4^d
I_3	983.2	605.7	121.6	2153.5	92.3 ± 4.7^d

^a Symmetry coordinates defined in Table V.

^b IR intensities for ¹⁶O₃; normal coordinates generated from experimental force constants.

^c Reference 99.

^d Reference 4.

consistent with our choice of signs. The resulting agreement between the CPF(ED) and experimental CDMDs is indeed very good. By extension, the IR intensities calculated at the CPF(ED) level are in good agreement with the best available intensities, those measured by Kim and King.⁹⁶ The calculated CPF(ED) dipole derivatives with respect to symmetry coordinates as well as the IR intensities are also compared with another set of experimental data, namely the IR intensities by Secroun and Jouve⁹⁸ and the corresponding derivatives, calculated by Strater and Smit.⁹⁷ Our calculated derivatives agree somewhat better with those based on the work of Kim and King,⁹⁶ although that may well be fortuitous. In conclusion, for SO₂ the single reference CPF expansion has been demonstrated to be capable of accurately predicting the main features of the dipole moment surface and yielding good quality IR intensities.

The situation, by now not unexpectedly, is found to be very different for ozone (Table VIII). Inspection of the SCF results shows that the derivatives involving μ_x are very large in magnitude and result in an order of magnitude overestimate for the intensity (I_3) of the antisymmetric (b_2) stretch. This problem is another manifestation of the one already discussed in the previous section: at the SCF level the ¹B₂-¹A₁ separation is severely underestimated and in analogy with the *xx* component of the polarizability, when the ¹B₂ state is allowed to mix with the ¹A₁ ground state as a result of the nuclear distortion, the magnitude of the resulting dipole moment in the *x* direction is too large. The dipole derivatives and IR intensities for the *a*₁ modes, viz. symmetric stretch and bend, are more reasonable; the accuracy of the calculated values is comparable with what was found for the dipole moment itself. On the basis of the above arguments we expect the single reference correlated calculations to yield reasonable results for the *a*₁ modes but to perform very poorly for the *b*₂ mode. This is confirmed by the results in Table VIII. For $\partial\mu_x/\partial S_3$ the CPF scheme has broken down completely as judged by the fact that the progression from SCF to CI to CPF is not at all what is observed in SO₂ where the near-degeneracy problems are far less severe, and that the (CPF)EV result (1.56) is very different from the ED value (-3.80).

Although it is clear that, for O₃, wave functions based on a single reference expansion are inadequate for the accurate calculation of quantities like α_{xx} and the intensity of the antisymmetric stretch, it is worth noting that the variational CI wave function still has the capability of resolving to a considerable extent the near-degeneracy that is present, provided the energy derivative formalism is used. It is pertinent to note also that a definitive theoretical study of the IR intensities of O₃ has already been carried out, by Adler-Golden *et al.*⁴ using the CASSCF method.

IV. SUMMARY AND CONCLUSIONS

The results of this study indicate that the ground state of sulfur dioxide at its equilibrium geometry can be adequately described by a single reference single and double excitation wave function and that the corresponding molecular properties are accurately predicted, provided the effects of quadruple and higher order excitations are taken into account, even if only in an approximate way. The CPF method,^{19,21} which is a size consistent generalization of the CI(SD) technique, appears to be well suited to this task, especially if the properties are evaluated as energy derivatives, as the non-Hellmann-Feynman contributions to a given property are found to be significantly greater than at the CI level. With the recent formulation of analytical energy gradients for CPF wave functions⁴³ it will be possible to calculate properties as energy derivatives far more efficiently than by the finite field method used in this work.

In the case of SO₂ agreement between the calculated [CPF(ED)] properties and the available experimental estimates has been found to be good. Enlargement of the basis set will undoubtedly change the theoretical predictions somewhat, although most of those changes are expected to affect the SCF values, rather than the correlation corrections. Thus, useful further work could be done at the SCF level using very large basis sets to obtain near Hartree-Fock estimates of one-electron properties. In addition to reproducing the properties whose values are well established experimentally, the current work has also made predictions of the field gradients at the oxygen atoms, where measurement

may be quite difficult, and clarified the sign of the dipole derivative with respect to the bending mode.

Compared with sulfur dioxide, ozone presents serious problems. It is less adequately described at the SCF level than SO_2 and, by extension, single reference correlated calculations also run into difficulties. The problem is most severe when mixing of the low lying 1B_2 excited state with the 1A_1 ground state can take place. As demonstrated, the energy separation in O_3 is poorly described at the SCF level, hence, in magnitude, properties such as α_{xx} and $\partial\mu_x/\partial S_3$ are seriously overestimated. In such situations a single reference CI(SD) wave function seems to be able to resolve the problems only partly, while the CPF (or CEPA) method is inapplicable as there are strong signs that the approximations inherent in CPF are breaking down. Thus, the current ozone results are judged to be considerably inferior to those for SO_2 . However, the important aspect and aim of the O_3 work has been to provide a basis of comparison with SO_2 and to emphasize the differences as well as similarities between the two molecules, rather than accurate theoretical predictions.

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