An ab initio SCF calculation of the polarizability tensor of sulphur dioxide

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NOTES

An *ab initio* SCF calculation of the polarizability tensor of sulphur dioxide

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The principal components of the dynamical polarizability tensor of SO_2 at the optical wavelength $\lambda = 5145$ Å have been recently determined experimentally by Murphy.[1] The procedure consisted of combining literature values of the average polarizability $(\bar{\alpha})$ and the Raleigh depolarization ratio[2] with possible values of the polarizability tensor component ratio so as to reproduce the Raman contours of the pure rotational spectrum of SO_2. Two sets of numerical values for the principal components are compatible with the results of the above experiments, corresponding to positive and negative values of the quantity $\alpha_{xx} - \bar{\alpha}$, where α_{xx} is the principal polarizability component along the dipole axis. As discussed by Murphy,[1] the negative sign for $\alpha_{xx} - \bar{\alpha}$ is the preferred one, partly on the basis of a negative Kerr constant,[3] provided the Kerr constant is not dominated by the first hyperpolarizability, and partly by intuition since the molecule is expected to be most polarizable along its bonds and least so perpendicular to the molecular plane.

In this note the results of an *ab initio* Hartree–Fock SCF calculation of the static polarizability $(\lambda = \infty)$ are presented which are believed to be sufficiently accurate to determine the sign of $\alpha_{xx} - \bar{\alpha}$ and decide in favor of one of Murphy's assignment for the polarizability tensor. In agreement with Murphy's choice, the sign of $\alpha_{xx} - \bar{\alpha}$ is found to be negative.

The components of the polarizability tensor were evaluated by the coupled perturbed Hartree–Fock (CPHF) method,[4-6] which is equivalent to the finite field Hartree–Fock method in the limit of vanishing applied electric field strength.[7] Briefly stated, the CPHF method allows the calculation of the first order change to the SCF occupied orbitals and the corresponding second order energy change within the Hartree–Fock formalism. In this work, as is the usual practice, the first order change to the doubly occupied orbitals is expanded in terms of the unperturbed virtual orbitals. The unperturbed SCF calculations were performed using the MOLECULE supermatrix package of Almlöf[8] and a new, symmetry blocked version of the quadratically convergent SCF (QC-SCF) program.[9] The same QC-SCF program was then used for the CPHF calculations, as already discussed in detail elsewhere.[9] The number of CPHF iterations needed per polarizability component was six to achieve six significant figure accuracy. The basis set for the S atom is the $(11s, 7p)$ Gaussian basis of Huzinaga,[10] contracted to $[6s, 5p]$ as recommended by Dunning and Hay,[11] except contracting the p's as $(3, 1, 1, 1, 1)$, and extended by a diffuse sp set $(\zeta = 0.05)$ and three sets of Cartesian $3d$ functions $(\zeta_1 = 0.60, \zeta_2 = 0.20, \zeta_3 = 0.07)$. The oxygen basis is Dunning's[12] $(9s, 5p)$ set contracted to $[4s, 3p]$ and extended by a diffuse sp set $(\zeta = 0.08)$ and two sets of Cartesian $3d$ functions $(\zeta_1 = 0.8, \zeta_2 = 0.2)$. Note that the $3d$ sets comprise of six functions i.e., the basis contains the $3s$ type $x^2 + y^2 + z^2$ orbitals, while the diffuse sp sets contain a $1s$ and the set of three $2p$ orbitals with the same exponent. The full contracted basis is thus $[7s, 6p, 3d; 5s, 4p, 2d]$, corresponding to a total of 101 basis orbitals. The diffuse s, p, and d functions were chosen in order to describe the polarizability adequately, as discussed in detail elsewhere,[14-20] while the $3d$ orbitals with the highest exponents are roughly optimal on energetic grounds.[17,21]

TABLE I. Results of the SCF and CPHF calculations for SO_2[a] and comparison with experiment.

Property	Calculated value	Experiment[b]	
Polarizability $(/Å^3)$[c]	$\lambda = \infty$	$\lambda = 5154$ Å	
$\bar{\alpha}$	3.506	3.9447 ± 0.001	
$\alpha_{xx} - \bar{\alpha}$	-0.437	-0.434	0.434
α_{xx}	3.069	3.511	4.379
α_{yy}	2.748	3.007	4.883
α_{zz}	4.701	5.317	2.572
Total energy (/hartree)			
This work	$-547.224\,711$		
Lindley[d]	$-547.240\,598$		
Huzinaga and Yoshimine[e]	$-547.224\,64$		
Dipole moment (/D)		$1.626\,73 \pm 0.000\,30$[f]	
This work	2.021		
Lindley[d]	2.04		
Huzinaga and Yoshimine[e]	2.33		

[a]Geometry for SO_2: C_{2v} symmetry, $r_{SO} = 1.432$ Å, $\theta = 119.5°$ [experimental (Ref. 24)].
[b]References 1 and 2.
[c]x is the dipole (C_2) axis and y is the axis perpendicular to the molecular plane.
[d]SCF value at optimized geometry, $r_{SO} = 1.404$ Å, $\theta = 118.8°$. Total energy obtained using $[8s, 6p, 2d; 5s, 3p, 1d]$ basis, dipole moment obtained using $[7s, 5p, 2d; 5s, 3p, 1d]$ basis (Ref. 22).
[e]SCF value at optimized geometry, $r_{SO} = 1.423$ Å, $\theta = 118.4°$, using $[6s, 4p, 1d; 4s, 2p, 1d]$ basis (Ref. 23).
[f]Reference 25.

The results of the calculations are summarized in Table I. Before a direct comparison is made with the experimental values it should be noted that for a given molecule the average static polarizability $\bar{\alpha}(0)$ is generally a few percent lower than those at finite frequencies.[13] An estimate of the experimental $\bar{\alpha}(0)$ may be obtained by using the empirical form of the Sellmeyer equation,[13] i.e., plot $\bar{\alpha}(\nu)$ against ν^2 and extrapolate to zero frequency $\nu = 0$. Such a procedure for SO_2 yields a value of 3.77 $Å^3$ for $\bar{\alpha}(0)$, i.e., ~5% lower than $\bar{\alpha}$ ($\lambda = 5145$ Å). Polarizability anisotropies show considerably less variation with frequency,[13] thus all principal components of the static polarizability are expected to be lower than the corresponding dynamical ones by approximately the same amount, while $\alpha_{xx} - \bar{\alpha}$ should show little frequency dependence. In light of the above, on comparing the calculated (static) polarizability component with the experimental (dynamical) set it is clear that the set for negative $\alpha_{xx} - \bar{\alpha}$ is the preferred one. The theoretical values consistently lie ~9%–12% below the experimental polarizability components although the differences would decrease to ~7% if the individual components were to be extrapolated too. We note that for a large range of atoms and molecules studied, SCF calculations (finite field or CPHF) with basis sets comparable to that used here, in the absence of near degeneracies, yield polarizability components that are generally 5%–12% below the corre-

lated values and experiment.[14-20] Thus SO_2 behaves very much as expected.

An independent set of relevant experimental values for SO_2 also exists, since the static polarizability anisotropies $\alpha_1 = \alpha_{zz} - \alpha_{xx}$ and $\alpha_2 = \alpha_{zz} - \alpha_{yy}$ in the vibrational ground state have been determined by Patel, Margolese, and Dyke through Stark effect measurements.[25] While the value of 1.64 ± 0.40 $Å^3$ for α_1 quoted by Patel et al. is in good agreement with the corresponding SCF value of 1.632 $Å^3$ and Murphy's 1.806 $Å^3$, their best estimate of α_2, viz. 0.1 ± 0.7 $Å^3$, is in considerable disagreement with both the SCF value of 1.953 $Å^3$ and Murphy's ± 2.310 $Å^3$. Patel et al. do comment on the difficulty of obtaining a reliable estimate of α_2, since depending on the rotational states used in fitting the Stark coefficient data α_2 shows considerable variation while α_1 remains relatively constant. Consequently the results of Patel et al. support, although less convincingly than the SCF calculations, the contention that $\alpha_{xx} - \bar{\alpha}$ is negative.

Except for the diffuse orbitals the basis set used in this work is of comparable quality to the most extended one used for SO_2 thus far, by Lindley,[22] who used a $[7s, 5p, 2d]$ contracted Gaussian basis on S and a $[5s, 3p, 1d]$ set on O extended by s and p Rydberg orbitals on S. Lindley's results are quoted for comparison in Table I as well as those of Huzinaga and Yoshimine[23] who used a double zeta plus polarization basis. As expected, the energy and dipole moment calculated by Lindley are in fair agreement with those obtained in this work. The difference in total energy is due to the fact that the exponents of the polarization functions used by Lindley, as well as his SO_2 geometry, were energy optimized. As noted already, the larger part of the polarization set used in this work was chosen with the polarizability in mind. In addition, the experimental, i.e., unoptimized geometry is used. The results of Huzinaga and Yoshimine[23] are somewhat inferior to those calculated here and to Lindley's,[22] especially with regard to the dipole moment which appears to be very sensitive to the choice of basis.

Further calculations on SO_2 are currently in progress and theoretical values of dipole and polarizability derivatives as well as a number of other electrical properties will be published in the near future.

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A classic example of an Evans hole caused by intermolecular interaction in solid 2ND₃·D₂O at 15 to 145 K

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It has recently been noted[1] that a sharp dip at 2333 cm^{-1} in the higher-frequency, infrared, O–D stretching band of 2ND$_3$·D$_2$O at 100 K may be an Evans hole.[2-5] In a study of the infrared spectra of the isotopic species 2NA$_3$·B$_2$O, where A and B are independently H or D, we have confirmed this possibility with evidence that is so unusually complete that we report it here, separate from the main body of our results.[6]

The methods used are described in detail elsewhere.[6,7] Briefly, NH$_3$ or ND$_3$, was co-condensed with H$_2$O or D$_2$O onto a cesium iodide plate held at 80 K in an Air Products, Displex, optical cell. Separate spraying nozzles were used for the ammonia and water, which were only mixed on the cold plate and had no opportunity for proton exchange. The sample composition, two parts of ammonia to one of water, was controlled by calibrated flow valves. The initial deposits were not crystalline, but crystallized without proton exchange at 125 K if their stoichiometry was correct.[7] That crystallization was complete at this temperature was confirmed by comparing the spectra of samples of 2NH$_3$·H$_2$O and 2ND$_3$·D$_2$O that were prepared in this way, and cooled to 100 K, with the spectra[1] of samples, at 100 K, that had been grown from the liquid and characterized by x-ray diffraction. Once a crystalline sample had been obtained, its spectrum was recorded for sample temperatures between 15 and 140 K. The sample thicknesses were of the order of 6 μm. The infrared spectra were recorded on a Nicolet 7199 FTIR spectrometer, at a nominal resolution of 1 cm^{-1} and using Happ–Genzel apodization. The frequency calibration of our instrument was accurate to at least 0.1 cm^{-1}.

The infrared absorption spectra between 2250 and 2450 cm^{-1} of 2ND$_3$·D$_2$O at temperatures between 15 and 140 K are shown in Fig. 1. The broad absorption has been assigned[1] to primarily the stretching vibration of the O–D bond of a D$_2$O molecule that is hydrogen bonded to the

type II ammonia molecule.[1,8] With decreasing temperature the peak frequency shifts from 2365 to 2322 cm^{-1}, while the dip shifts only from 2335.5 to 2332.5 cm^{-1}. At the two higher temperatures, the shape of the band allows the possibility that a peak at 2330 or 2327.5 cm^{-1} is superimposed on the broadband. However, the spectra at 50 and 15 K clearly indicate that the dip in the band is the superimposed feature, i.e., that the dip is a hole
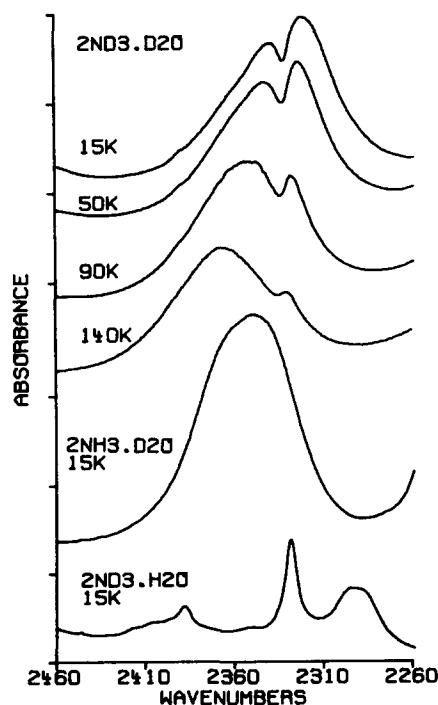

FIG. 1. Infrared spectra of 2ND$_3$·D$_2$O, 2NH$_3$·D$_2$O, and 2ND$_3$·H$_2$O at 1 cm^{-1} resolution and the sample temperatures shown.