



The electronic structure of SiO_3 : a problematic example for coupled cluster methods

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Abstract

A new Si_xO_y species has been isolated in argon matrices at low temperatures by Roy et al. [J. Chem. Phys. 104 (1996) 8]. The new species was characterized by vibrational spectra and proposed to be SiO_3 in a C_{2v} structure, with an unusual O–O bond. To explore this structure, we use the CCSD(T), QRHF-CC, EOM-CC, IP-STEOM and the DIP-STEOM method to investigate SiO_3 and its anion. The IP-STEOM and DIP-STEOM schemes allows us to describe traditional multi-reference situations in what is conceptionally a one determinantal frame work. Our results support the experimentally found C_{2v} structure.

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1. Introduction

The Chemistry of silicon oxides is important technologically. Recently the hydrolysis of the amorphous silica surface has been studied theoretically [2,3]. The work indicates that there are four basic types of chemical environment for silicon in amorphous silica, two of which are three-coordinated local defect structures found on the surface. To understand the reactivity on the surface, the electronic structure of the unsaturated three-coordinated species is important, an indication of which can be given by gas phase studies on SiO_3 .

Furthermore, efforts have been made to avoid the high temperature and high pressure conditions

necessary for the oxidation process of silicon using molecular oxygen [4]. In this context, studies of the geometrical and electronic structure of the various molecular silicon oxides as well as of their reactivities and their access via alternative reaction channels are pertinent.

Ogden et al. [5] isolated SiO , Si_2O_2 and Si_3O_3 by matrix isolation starting from evaporated SiO . Schnoekel et al. [6,7] were able to produce molecular SiO_2 by the reaction of SiO vapor with atomic oxygen generated in a microwave discharge. Also the dimeric species Si_2O_4 was found by the same group by the photolysis of Si_2O_2 and O_2 aggregates [8]. Andrews and McCluskey [9] studied the reaction of laser-ablated silicon with molecular oxygen in solid argon yielding SiO_2 .

In the work of Schnoekel [6,7] an interesting weak IR-band appeared at 1363.2 cm^{-1} which could not be assigned to any known silicon oxide

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species. The same band at 1363.3 cm^{-1} was also seen by Andrews and McCluskey [9]. The new band was thought to belong to an unidentified Si_xO_y species. To identify the unknown species Roy et al. [1] studied the reaction of Si and SiO with oxygen further.

The new species could be produced by condensation of silicon with O_2 in solid argon and subsequent irradiation by the Hg emission line at 240 nm. Roy et al. observed nine new bands, among them the one in question at 1363.5 cm^{-1} . The same bands but with higher intensities appeared when SiO was condensed with O_2 in solid argon followed by irradiation at 240 nm. The new species was proposed to be SiO_3 and characterized by the vibrational spectra of eight different isotopic species. The experimental data suggested a structure of C_{2v} symmetry with a Si–O double bond and two equivalent Si–O single bonds. To support the structure deduced by experiment, Roy et al. performed DFT calculations and found a C_{2v} equilibrium structure for SiO_3 . The frequencies were computed by a semi-empirical molecular force field calculation based on the DFT geometry.

However, only 5 out of the 9 observed frequencies could be assigned to the theoretically predicted values for SiO_3 and a theoretical predicted A_1 vibration could not be found in the experimental data. This raised questions about the electronic structure of the SiO_3 species. The C_{2v} closed shell structure assumes an oxygen–oxygen bond in a ring of three atoms. Although this type of ring structure is very well known for transition metal complexes $\text{O}_2\text{--M}$, the bonds in silicon compounds are expected to be of covalent nature which would cause the oxygen–oxygen bond in a 3-ring to be under tension. An opening of the oxygen–oxygen bond results in an open shell singlet structure which should be considered but which is not accessible with traditional one determinantal approaches. On the other hand if SiO_3 can be regarded as a complex consisting of a SiO and a O_2 unit which also avoids the tension in the ring structure, SiO_3 might be a triplet. An alternative symmetry for SiO_3 is a D_{3h} symmetry. A simple Hartree–Fock calculation for the D_{3h} structure of SiO_3 gives the qualitative orbital picture shown in Fig. 1. The D_{3h} structure seems to be

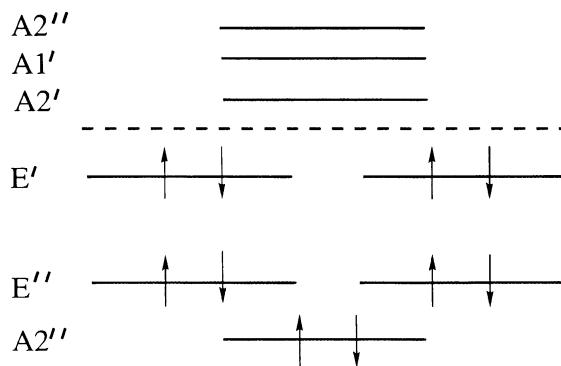


Fig. 1. Orbital diagram of SiO_3 in D_{3h} symmetry.

a perfectly reasonable candidate for the electronic structure of SiO_3 , Fig. 1 does not indicate a Jahn Teller distortion due to partly occupied degenerate highest orbitals. However, a MBPT(2) calculation of the D_{3h} structure shows very large weights of the doubly excited determinants in the wave function. Fig. 2 shows the orbital picture of SiO_3 in C_{2v} symmetry obtained from a Hartree–Fock calculation where the geometry was only slightly distorted from the D_{3h} symmetry. In the C_{2v} symmetry an excitation from the highest occupied orbital into the lowest unoccupied orbital is symmetry allowed ($B_2 \rightarrow B_2$) whereas it is not for the D_{3h} structure ($E' \rightarrow A_2'$) which explains the high amplitudes for the doubly excited determinants in a MBPT(2) calculation in D_{3h} symmetry indicating that at least one other determinant than the Hartree–Fock reference function is important to describe the ground state. Therefore, traditional one determinantal approaches are less appropriate to describe the system in D_{3h} symmetry.

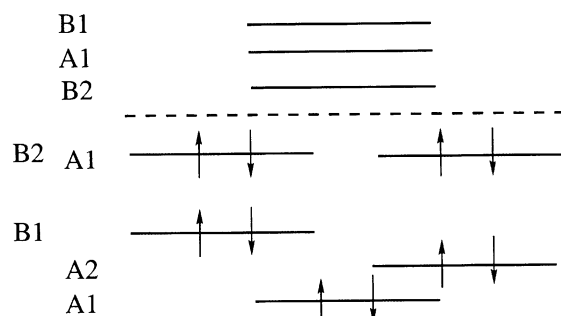


Fig. 2. Orbital diagram of SiO_3 in C_{2v} symmetry.

We also want to consider the possibility that the species in question is the anion SiO_3^- since the experimental conditions might allow for high energy processes like electron transfer. However, we dismissed the D_{3h} symmetry for SiO_3^- since the wave functions calculated with the Hartree–Fock methods is not symmetric for all doublet states. Additionally the point group changes to C_{2v} symmetry during IP-STEOM-CC calculations of all doublet state. We therefore concentrated our efforts concerning the anion on the C_{2v} structure.

In the following, we consider several aspects of the structure of SiO_3 and SiO_3^- using sophisticated coupled cluster methods for ground and excited states. SiO_3 and SiO_3^- are difficult examples that illustrates several of the limitations of various correlated theories.

2. Theory

Besides the usual single reference ground state methods like CCSD(T), in this study we also use the equation-of-motion coupled cluster (EOM-CC) method for excited states, the ionization potential (IP-STEOM-CC) method, the double ionization potential (DIP-STEOM-CC) method and the QRHF method to access states that differ by one or two electrons from a reference state.

In the EOM-CC method [10–13], excited states are created in a CI like spirit but the reference state corresponds to a coupled cluster wave function providing a good description for the excited state. The excited state wave functions are eigenstates of the transformed Hamiltonian \bar{H} .

$$\bar{H} = e^{-T} H e^T. \quad (1)$$

In the case of EOM-CCSD $T = T_1 + T_2$, the singles and doubles connected excitation operators obtained from a standard CCSD calculation. The method gives direct access to accurate excitation energies in a very effective way. An EOM-CCSD calculation of SiO_3 at the optimum geometry of a reference state would therefore immediately show if there are lower lying excited (or dexcited) states in that geometry, discriminating whether the state is an excited state or a ground state.

In the similarity transformed equation-of-motion coupled cluster scheme (STEOM-CC) [14–16] a second similarity transformation of the Hamiltonian is performed. The transformation is chosen such that the one- and two-body components that net increase the excitation level are transformed to zero. The final Hamiltonian

$$G = \{e^S\}^{-1} \bar{H} \{e^S\}, \quad (2)$$

is approximately in block form which makes it very easy to determine its eigenvectors. Each block corresponding to an excitation level can be diagonalized separately. Within the STEOM-CC scheme excitation energies of states with dominantly single excitation character can be obtained by diagonalizing G in the subspace of singly excited determinants, in the EOM-CC framework \bar{H} has to be diagonalized in the subspace of singly and doubly excited determinants, and for even higher accuracy triple excitations have to be included (EOM-CCSDT). To determine the coefficients of the second transformation operator $\{e^S\}$ the EOM-CC problem for the IP and EA sectors has to be solved. This constitutes an eigenvalue problem in the space of 1h-2h1p configurations and the space of 1p-2p1h configurations, respectively. The second transformation which results in vanishing hhhp and hppp components in the final Hamiltonian also results in an implicit inclusion of triple excitation effects which leads to more accurate excitation energies for singly excited states.

A very useful application of the STEOM-CC scheme is the calculation of ionization spectra. The excited state can as well have 1 or 2 electrons less than the ground state which defines the ionized or the doubly ionized similarity transformed equation-of-motion coupled cluster method (IP-STEOM-CC/DIP-STEOM-CC). It can be used to obtain highly economical descriptions of traditional multi-reference situations with an operational one determinantal approach. If the parent state can be described by a closed-shell determinant with 1 or 2 more electrons, removing those electrons yield a linear combination of reference determinants. Therefore, in order to access all the above described possible structures of SiO_3 one can perform a DIP-STEOM-CCSD calculation of SiO_3^{2-} which can be well described by a closed-shell

single determinant as the reference, and then remove two electrons to describe SiO_3 . The structure of SiO_3^- can be determined by removing one electron from SiO_3^{2-} in an IP-STEOM-CC calculation. Apart from the fact that IP-STEOM-CC and DIP-STEOM-CCSD calculations are by far less costly than a multi-reference CI calculation, practical difficulties like choosing an appropriate active space are avoided. Choosing an active space in a multi-reference calculation can be ambiguous or dependent on the particular system, the method used, and the basis set, leading to a trial and error scheme. The DIP-STEOM-CC method has been successfully applied to treat difficult cases like ozone [16] and transition states on the potential surface of NO_4^+ [17] and N_8 [18]. The IP-EOM method was used to calculate benchmark ionization potentials of ethylene as well [19].

Another possible route to access electronic states which show symmetry-breaking problems is to perform a coupled cluster calculation in which a quasi-restricted open-shell (QRHF) reference function is used [20]. The QRHF method exploits the fact that the coupled cluster method is not very sensitive to the choice of orbitals since the function of e^{T_1} is to adjust the orbitals. If a state with an added or subtracted number of electrons relative to the state of interest can be reasonably well described by a closed shell single determinant then a Hartree–Fock calculation can be performed on that state to obtain a reference function from which electrons are removed or added using appropriate occupation numbers. The orbitals can be used for the subsequent coupled cluster calculation. In cases of severe symmetry breaking the QRHF reference function can be more suitable than a UHF or ROHF reference as indicated by the fact that the largest T_1 amplitudes can be a magnitude smaller when the QRHF reference is used. Since the SiO_3^{2-} can be reasonably well described by a single determinant it can be used as a reference function in a QRHF calculation. Removing one electron and performing a subsequent coupled cluster calculation delivers SiO_3^- , removing two electrons results in the neutral species SiO_3 . The QRHF-CCSD method has been successfully applied to C_3^+ [21], the NO_2 [22] radical and the NO_3 [23,24] radical.

3. Computational details

The two points of interest for the SiO_3 molecule are the potential C_{2v} and D_{3h} symmetries. Geometry optimizations for the C_{2v} singlet and triplet states are performed at the CCSD(T) level of theory. At the D_{3h} symmetry the geometries for the singlet and triplet state are computed with the DIP-STEOM-CCSD method since the multi-reference character of the system does not allow straightforward single determinant CCSD(T) calculations. For the excited state calculations in C_{2v} symmetry the optimized CCSD(T) geometries are used.

The C_{2v} doublet structure of the anion SiO_3^- is investigated with the IP-STEOM-CCSD method. For the neutral species and the anion a QRHF calculation on the CCSD(T) level is done using SiO_3^{2-} as a reference function.

For consistency between excited and ground states, the Sadlej basis set [25] is chosen. It contains 5s, 3p and 2d contracted Gaussians for the oxygen atom and 7s, 5p and 2d contracted Gaussians for the silicon atom. The Sadlej basis set has sufficiently diffuse character to describe the anion well, though it might be less sensible for the neutral ground state description.

For refined calculations we use the cc-pVTZ basis set for the CCSD(T) calculation of the C_{2v} singlet structure of SiO_3 . A single point Hartree–Fock calculation of the C_{2v} doublet structure of SiO_3^- shows that there is little diffuse character for the anion, since the lowest occupied molecular orbitals lies at -3.92 eV. We therefore use the cc-pVTZ basis set to obtain reliable frequencies of SiO_3^- in an IP-STEOM-CCSD calculation. We use the cc-pVTZ basis set as well to perform QRHF-CC calculations on the neutral SiO_3 and the anion SiO_3^- .

All calculations employ the ACES II package.

4. Results

In our first attempt to determine the geometrical and electronic structure of SiO_3 we perform single determinant CCSD(T) calculations at the C_{2v} and D_{3h} symmetry. The geometry of the closed

shell singlet in C_{2v} symmetry is readily obtained but the triplet state in C_{2v} is problematic. The amplitudes for the C_{2v} triplet are fairly high with the largest T_1 amplitude being 0.15 and the largest T_2 amplitude -0.09 . Amplitudes larger than $|0.10|$ are considered to be high calling into question whether the wave function should be described by a single reference CC calculation. These problems manifest themselves also in the frequency calculation where sudden switches in the SCF state occur. The optimized geometries are given in Fig. 3 and the calculated energies in Table 1.

It is not possible to obtain the D_{3h} singlet nor the triplet within the usual single determinant framework of a CCSD(T) calculation. Amplitudes as high as -0.25 for the T_2 amplitude of the singlet and 0.26 for the T_1 amplitude of the triplet state show that one can not trust such results.

However, we obtain the D_{3h} singlet and triplet structures with the DIP-STEOM-CCSD method. The geometries are shown in Fig. 3 and the energies in Table 1. We also tried to optimize the C_{2v} geometries for the singlet and triplet state with the DIP-STEOM-CCSD scheme. We found large T_2 amplitudes of -0.21 for the singlet and we run into

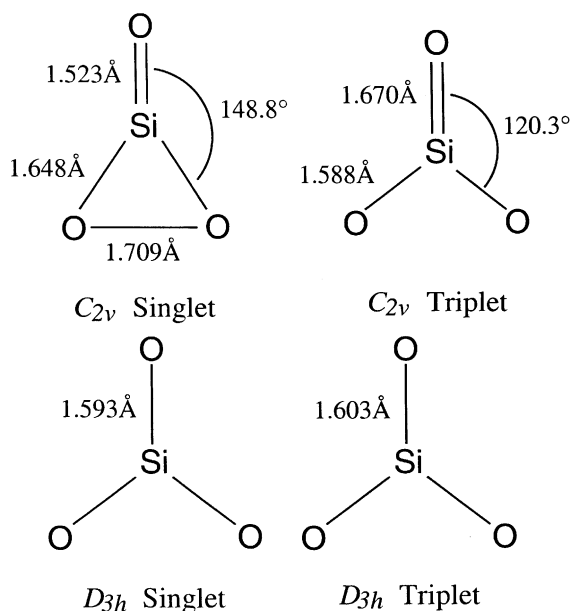


Fig. 3. Calculated geometrical parameters of SiO_3 .

serious SCF convergence problems for the triplet. This shows that the basic assumption for the STEOM-CC approach to be valid is not well fulfilled. The reference state needs to be well described at the single determinant level so that the correlation effects are mainly dynamical. The SiO_3^{2-} ion is well described as a closed shell singlet in D_{3h} symmetry, but the artificial distortion into C_{2v} symmetry results in a poor description of the ion at the SCF level.

The possibility of an open shell singlet at the D_{3h} symmetry is taken into account by the DIP-STEOM-CCSD method whereas this is not the case for the CCSD(T) calculation at the C_{2v} point where we only consider a closed shell singlet. In order to exclude the open shell singlet in C_{2v} symmetry we perform an excited state EOM-CCSD calculation at the optimized CCSD(T) geometry. It is found that the lowest-lying open shell singlet is a B2 singlet and is 68.5 kcal/mol higher in energy than the closed shell singlet. This is a considerably higher energy and the open shell singlet can therefore be excluded.

As can be seen in Table 1, the energy for the C_{2v} closed shell singlet is the lowest. The optimized C_{2v} triplet structure has the next lowest energy but is 22.5 kcal/mol higher in energy.

At this point, the question of comparability of the CCSD(T) and the DIP-STEOM-CCSD method should be addressed. Both methods are based on the exponential ansatz of the wave function. The CCSD(T) method exploits that fact fully (through T_1 and T_2 ; approximately for T_3) whereas in the DIP-STEOM-CCSD method only the anion fully benefits from the exponential in $T_1 + T_2$. In calculating the neutral species, orbital relaxation effects are neglected. Bartlett et al. [26] studied electron affinities with the Δ CCSD and with the IP-EOM-CCSD method. The IP-EOM method yields electron affinities that are only 2–5 kcal/mol higher than the Δ CCSD electron affinities. It has been surmised that this difference is caused (1) by the neglect of orbital relaxation and (2) the difference in the exponential character. Furthermore, in a recent study on ethylene [19] it was found that the ionization potentials obtained with the Δ CCSD(T) method and the IP-EOM-CCSD method are very close, the largest absolute differ-

Table 1
Energies and relative energies of the different SiO₃ structures

Symmetry	Spin state	Irrep	<i>E</i> [H]	ΔE (kcal/mol)
C _{2v}	singlet	A1	-514.30715	0.0
C _{2v}	triplet	A2	-514.27135	22.5
D _{3h}	singlet	A1'	-514.26780	24.7
D _{3h}	triplet	E''	-514.26754	24.9

ence being 3.7 kcal/mol. The partial inclusion of triples in the CCSD(T) method is therefore expected to not have a large effect on the total energies. As an example we calculated the energy of water with the CCSD(T) and the DIP-STEOM-CCSD method. For both calculations the 6-31G** basis set was used. The energy difference was 5.2 kcal/mol. Since for SiO₃ the calculated energy differences to the C_{2v} closed shell singlet are over 20 kcal/mol we conclude that the error we make does not affect our overall result.

The four possible states of the C_{2v} doublet structure of SiO₃⁻ are readily obtained with the IP-STEOM-CCSD method. The relative energies are given in Table 2. The B2 doublet state lies lowest in energy. The geometry of the B2 state is shown in Fig. 4.

We also tried to calculate the structure of the anion SiO₃⁻ with the CCSD(T) method. However, the geometry optimization leads to states where the Hartree–Fock SCF procedure fails to converge and the wave function shows *T*₁ amplitudes as high as 0.96. The high *T*₁ amplitudes show that the reference function is ill chosen and the problem might be solvable with a QRHF calculation. We perform a QRHF calculation on the CCSD(T) level using the Slater determinant of SiO₃²⁻ obtained by a Hartree–Fock calculation as a reference function, remove one electron and proceed with the CCSD(T) calculation to compute the B2

Table 2
Energies and relative energies of the different SiO₃⁻ states

Irrep	<i>E</i> [H]	ΔE (kcal/mol)
B2	-514.43545	0.0
B1	-514.40854	16.9
A2	-514.40406	19.7
A1	-514.38139	33.9

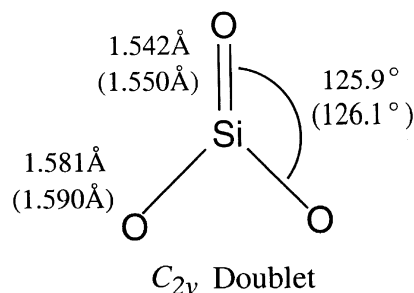


Fig. 4. Calculated geometrical parameters of SiO₃⁻ with IP-STEOM-CCSD, QRHF values in parenthesis.

state of SiO₃⁻. The optimized geometry can be found in Fig. 4. However, the frequency calculation shows that the QRHF method could only partly resolve the problem of the multi-reference character in the SiO₃⁻ system. In the numerical frequency calculation the atoms have to be displaced which might lower the symmetry depending on the frequency mode which is calculated. When the symmetry is lowered to C_s symmetry the wave function has high weights of doubly excited determinants, the highest *T*₂ amplitude being -0.25, which is an indication of the multi-reference character. The A1 frequencies are given in Table 3.

An attempt to calculate the neutral species SiO₃ with the QRHF method fails because the geometry optimization yields a state where the Hartree–Fock SCF procedure does not converge. This shows again that the SiO₃²⁻ reference function is of poor quality when the molecule is distorted to C_{2v} symmetry. Comparing the geometries of the C_{2v} singlet structure of SiO₃ and the C_{2v} doublet structure of SiO₃⁻ in Figs. 3 and 4 shows that the extent of distortion is far less in SiO₃ than it is in SiO₃⁻ which explains the fact that the C_{2v} structure of SiO₃⁻ can be described by the IP-STEOM-CCSD and to a certain degree by the QRHF

Table 3

IP-STEOM-CCSD/cc-pVTZ and QRHF-CCSD(T)/cc-pVTZ frequencies of the B2 doublet state of SiO_3^- , experimental frequencies from [6], the intensities are given in parenthesis

Symmetry	Experimental frequencies	IP-STEOM-CCSD	QRHF
B1	287.8 (96)	417.1	–
B2	292.0 (62)	69.1	–
A1	–	203.3	200.5
B2	855.3 (53)	860.9	–
A1	877.1 (12)	908.4	878.9
A1	1363.5 (100)	1197.9	1174.9

method, whereas the SiO_3^{2-} reference function becomes too poor, with further distortion, to describe the neutral species SiO_3 .

The frequencies of the B2 doublet state of the anion SiO_3^- are given in Table 3. Note, the frequencies differ very much from the experimentally found ones, especially for the low lying B1 and B2 frequencies. We conclude that the experimentally investigated species is not the anion SiO_3^- .

To identify the experimentally observed species we compare the calculated frequencies of the C_{2v} singlet structure with the experimental values, see Table 4. The calculated frequencies are in good agreement to the experimental values in general. The calculated B1 frequency is overestimated (by 12.1%), which is rather a lot compared to the other frequencies for which the deviation to the experimental value falls between 0.5% and 2.1%. However, low frequencies are harder to describe since they correspond to flat potentials where the minimum is harder to find and the harmonic approximation is less justified. It is surprising that the A1 frequency at 506.9 cm^{-1} is not observed by the

Table 4

CCSD(T)/cc-pVTZ frequencies of the C_{2v} singlet SiO_3 structure, experimental frequencies from [6], the intensities are given in parenthesis

Symmetry	Experimental frequencies	CCSD(T)	Deviation (%)
B1	287.8 (96)	322.7 (72)	12.1
B2	292.0 (62)	290.6 (49)	0.5
A1	–	506.9 (15)	–
B2	855.3 (53)	864.0 (15)	1.0
A1	877.1 (12)	889.6 (5)	1.4
A1	1363.5 (100)	1392.2 (100)	2.1

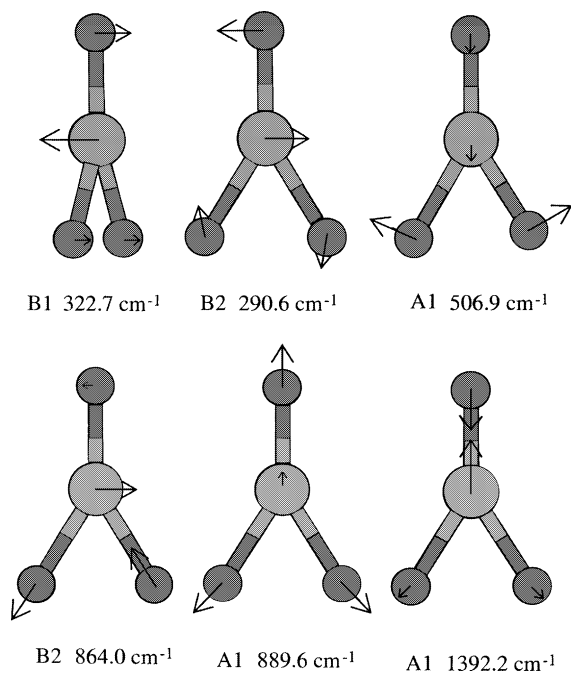
experiment. This frequency has an intensity of 15% relative to the highest peak in the spectrum whereas a frequency which is predicted to have an intensity of 5% is observed.

In Table 5 we summarize our results for the frequency calculations of the isotopes of SiO_3 . The differences between the experimental frequencies of the two isotopes and the calculated frequencies agree very well and are given in the last two columns. The difference of the isotopic frequencies is typically a more reliable indication of assignment than are the absolute values. The A1 frequency at 877.1 cm^{-1} was mainly assigned to an oxygen–oxygen stretching mode by Roy et al. Fig. 5 shows the frequency mode analysis of SiO_3 . It can be seen that this frequency has indeed a high oxygen–oxygen stretching mode contribution and is therefore expected to be uninfluenced by isotope effects. Experimentally the isotopic difference of this frequency is 0.0 cm^{-1} compared to the calculated frequency 0.4 cm^{-1} . The lowest A1 frequency at 507.4 and 506.8 cm^{-1} , respectively, which was experimentally not observed, also shows little

Table 5

CCSD(T)/cc-pVTZ isotopic frequencies of the C_{2v} singlet SiO_3 structure, experimental frequencies from [6]

Symmetry	$^{29}\text{Si}^{16}\text{O}_3$		$^{30}\text{Si}^{16}\text{O}_3$		ΔExp	ΔCC
	Experimental frequencies	CCSD(T)	Experimental frequencies	CCSD(T)		
B1	285.2	308.5	282.6	305.4	2.6	3.1
B2	290.1	245.8	–	244.5	–	1.3
A1	–	507.4	–	506.8	–	0.6
B2	851.6	797.5	848.2	793.6	3.4	3.9
A1	877.1	884.2	877.1	883.8	0.0	0.4
A1	1351.2	1369.9	1339.6	1357.8	11.6	12.1

Fig. 5. Frequency mode analysis of SiO₃.

influence due to isotope effects. Fig. 5 shows that the lowest A1 frequency also has a high contribution of an oxygen–oxygen stretching mode, which explains the small value for the difference in frequency between the isotopic SiO₃.

5. Summary

The recently isolated new Si_xO_y species [1] was studied theoretically with a range of very accurate and highly sophisticated computational methods since the previously performed DFT calculation [1] could not be applied to all alternative electronic structures, and since only an empirical force field was used to obtain the frequencies. We used CCSD(T), EOM-CC, IP-STEOM, DIP-STEOM and QRHF-CC methods to treat open and closed shell singlet and triplet electronic structures of SiO₃ in C_{2v} and D_{3h} symmetry as well as the C_{2v} doublet states of SiO₃⁻. The wide variety of methods was necessitated by the difficulty in describing the system. The IP-STEOM and DIP-STEOM methods allow us to study systems with multi-

reference character in what is conceptually and operationally a single determinantal approach. We excluded the possibility that the experimentally investigated species is the anion SiO₃⁻. We found that the energetically lowest lying SiO₃ state is the closed shell singlet C_{2v} structure which confirms the experimentally identified structure. We also computed the frequencies of the singlet C_{2v} structure and found good agreement with experiment. We identified an unobserved vibrational A1 mode at 506.9 cm⁻¹ which has a strong contribution from the oxygen–oxygen stretching mode. The intensity of that mode is fairly high and should have been visible in the spectrum.

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