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A Further Study of the Products of Scandium and Dioxygen Reactions

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The products of the reaction of Sc and dioxygen have been reinvestigated. By adding the electron-trapping molecule CCl_4, additional information about the IR spectra has been obtained, as well as the observation of new bands. New ab initio calculations are also performed on possible products of the Sc plus O_2 reaction. The previously observed band at 722.5 cm^{-1} is assigned as the b_2 mode of ScO_2^-. Bands arising from ScO^+, $Sc(O_2)^+$, and(O_2)ScO are also assigned. We are still unable to assign any bands to OScO. The problems associated with the computational study of ScO_2 are discussed.

Introduction

The reactions of laser-ablated first transition row atoms with dioxygen have been extensively studied.[1] We have found that synergistic effects are achieved by combining theory and experiment for the identification of the products. This has allowed us to identify many unexpected species with confidence. It has also been very encouraging that relatively low-level approaches, such as density functional theory[2,3] (DFT), have performed very reliably. This allows the computational study of species on the same time scale as experiment. However, simple computational approaches may not always succeed; we recently noted[4] that harmonic frequencies of the $^2B_2$ state of ScO_2 were very sensitive to the level of theory used, with some levels of theory yielding a molecule with two equivalent Sc−O bonds (i.e. C_{2v} symmetry) and other levels yielding a C_s structure with two inequivalent Sc−O bonds. Perhaps the most surprising finding of that study was the large difference between experiment and the computed results obtained using the high level coupled cluster singles and doubles approach,[5] including the effect of triples[6] using perturbation theory (CCSD(T)). The CCSD(T) harmonic frequencies for the a_1 and b_2 stretching modes were 745 and 604 cm^{-1}, respectively, and their $^{16}O/^{18}O$ isotopic ratios were 1.0554 and 1.0362. One band was observed in experiment[1a] at 722 cm^{-1} with an isotopic ratio of 1.0367. Since the computed isotopic ratios are usually more reliable than the frequencies, the experimental band was assigned as the b_2 mode of ScO_2, thus suggesting the CCSD(T) frequency was in error by 118 cm^{-1}, which is far larger than expected for this level of theory. In this manuscript we reinvestigate ScO_2 and related species using experiment and several computational techniques. We identify several new species and we show that the band previously assigned as ScO_2 actually comes for ScO_2^-. The continuing experimental and computational problems with ScO_2 are also discussed.

Experimental Methods

With the same apparatus and techniques as described in our previous study,[1a] new experiments were performed using lower laser power (1−5 mJ/pulse) and doping with the electron-trapping molecule CCl_4 at 10% of the O_2 reagent concentration.

Computational Approaches

Part of this work builds on our previous studies[1a,4] and hence the same computational methods are used. Most of the systems are studied using the DFT approach, where we use the BP86[7,8] and hybrid[9] B3LYP[10] functionals in conjunction with the oxygen 6-31+G* basis set[11] and a (14s11p6d)/[8s6p4d] Sc set,[12−13] which has been described in detail previously.[4] We also use the 6-311+G(2df) set for oxygen[11] and the 6-311G(d) set for Sc;[12−14] we denote these larger sets "L". The harmonic frequencies are computed analytically.

For ScO_2 and ScO_2^-, the more rigorous restricted CCSD(T) approach is used to treat the correlation problem. These calculations are based on a spin-restricted self-consistent-field (SCF) approach. These calculations use the same basis set as our previous study;[4] for oxygen this is the augmented-correlation-consistent polarized valence triple-ζ (aug-cc-pVTZ) set,[15,16] while for Sc it is the 3s3p modified (21s16p9d6f4g)/[7s8p6d3f2g] averaged atomic natural[17] (AANO) set described previously.[4] To test the effect of further basis set expansion on the computed vibrational frequencies of ScO_2, CCSD(T) calculations are

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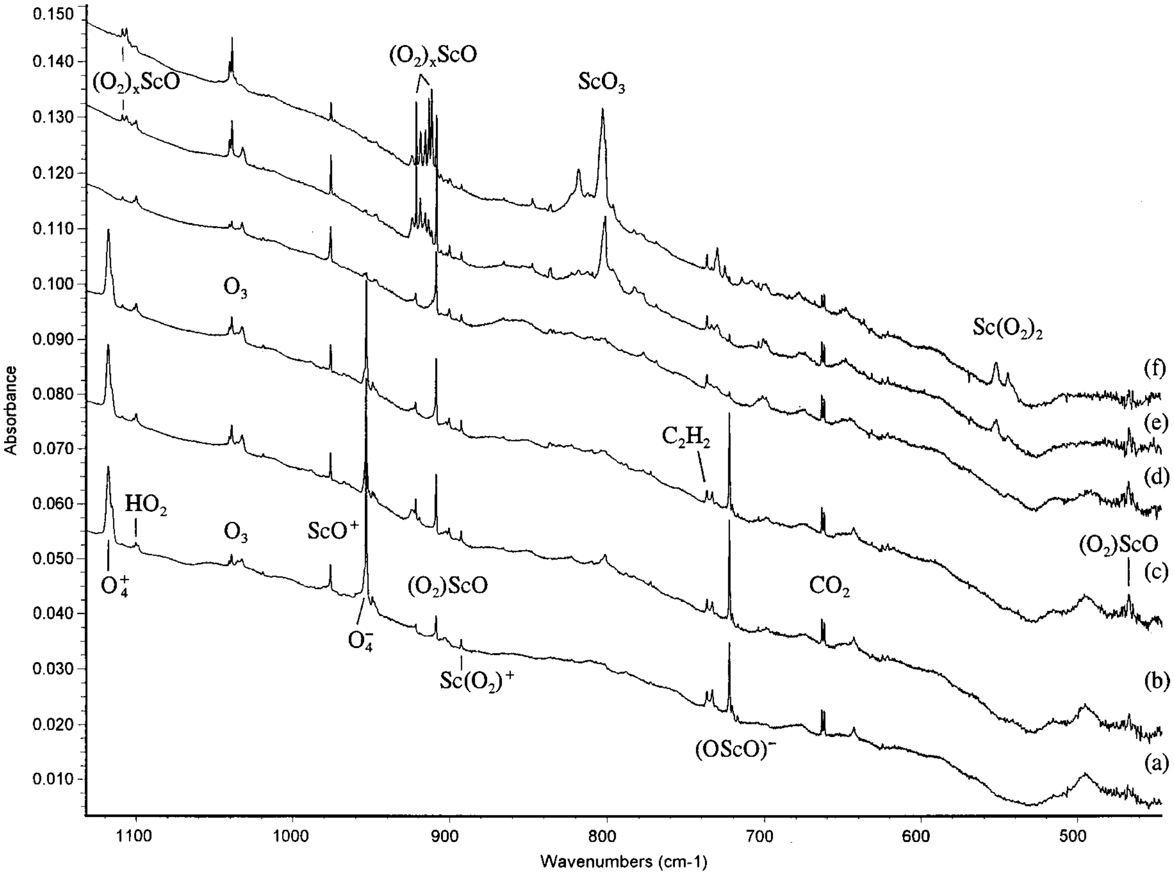

Figure 1. Infrared spectra in the 1130−450 cm^{-1} region for laser-ablated Sc codeposited with 0.5% O_2 in argon. (a) sample collected for 1 h at 10 K, (b) after annealing to 20 K, (c) after λ >470 nm photolysis, (d) after full-arc photolysis, (e) after annealing to 25 K, and (f) after annealing to 30 K.

performed using an even bigger basis set, which we denote as “B”; for oxygen, the aug-cc-pV quadruple-ζ (QZ) set is used, while for Sc, the previous set is supplemented with two additional f functions (with exponents of 1.6 and 0.67) and an h function (0.3). In the CCSD(T) calculations, the geometries are optimized and the harmonic frequencies computed using numerical first and second energy derivatives.

For ScO_2, ScO_2^+, and ScO_2^-, the complete active space (CAS) SCF approach is used as the zeroth order wave function and dynamic correlation is added using multiconfigurational second-order perturbation theory (CASPT2).[18,19] Geometries were optimized by pointwise calculations at the CASPT2 level and the resulting points were fit to second-order polynomial in two (C_{2v}) or three (C_s) degrees of freedom. Harmonic vibrational energies were obtained from the force constant obtained in the fit.

In the CASPT2 calculations, the basis set used was the ANO[20,21] with [6s5p3d2f] functions for Sc and [4s3p2d] functions for O. Primitive functions were added for Sc to describe correlation of the 3p electrons: three s-type functions (exponents of 0.94, 0.42, and 0.10), three p-type functions (2.59, 1.20, and 0.53), three d-type functions (3.90, 1.80, and 0.75), and one f-type function (1.65).

The active space for ScO_2^+, ScO_2, ScO_2^- comprised 12 orbitals with 10, 11, or 12 electrons, respectively. These orbitals can best be described as the 2p and 3p orbitals of the oxygen atoms, even if they contain a substantial amount of Sc 3d. The most important radial correlation effects for the oxygen 2p electrons are thus included already at the CASSCF level of theory. All orbitals were optimized at the CASSCF level, while the Sc 1s2s2p shells and the O 1s shells were kept frozen in the CASPT2. Thus the same electrons are correlated in the CCSD(T) and CASPT2 calculations.

The DFT calculations were performed using GAUSSIAN 94,[22] the CCSD(T) calculations with MOLPRO[23] and the CASPT2 calculations with MOLCAS4.[24]

Experimental Results

New experiments were done as described previously[1a] using much lower laser power and 0.5% O_2 in argon. The product bands are in general weaker and the relative populations are different from our previous study, as can be seen in Figure 1. Most notably, the O_4^+ and O_4^- bands[25] at 1118.4 and 953.7 cm^{-1} are stronger, which means that charged species are trapped more efficiently with lower laser power (and less intense radiation from the laser plume on the target surface). The earlier experiment gave the 722.5 cm^{-1} band 1.4 times more intense than the 909.0 cm^{-1} band, but in the present matrix, the 722.5 cm^{-1} band is 3 times more intense. The earlier experiment gave approximately equal 976.3 and 954.8 cm^{-1} bands, but the present experiment gave 976.3 cm^{-1} twice as intense. The 0.5% O_2 experiment was repeated with the same low laser power, but with 0.05% CCl_4 added to serve as an electron trap, and the resulting spectra are illustrated in Figure 2. Several bands, such as CCl_3^+, $CCl_3{-}Cl$ and CCl_3, are common to CCl_4 experiments with other metals.[26] Although O_4^+ has been reduced, O_4^- has been virtually eliminated, and the 722.5 cm^{-1} band reduced to <10% of its former absorbance and the 892.9 cm^{-1} absorption increased 5-fold. The 976.3 cm^{-1} band absorbance is not charged, but the relative yeild of ScO^+ to ScO(shoulder under O_4^-) is increased. Furthermore, photolysis

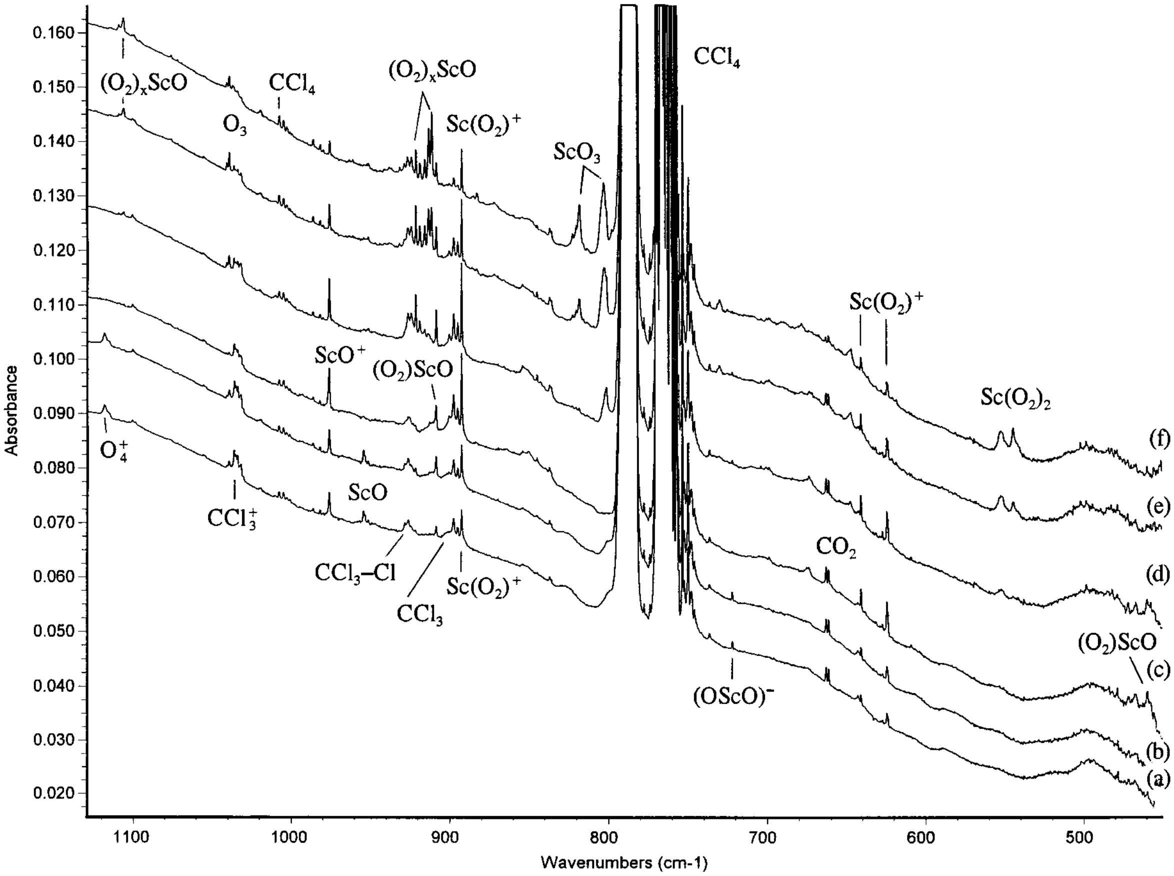

Figure 2. Infrared spectra in the 1130−450 cm^{-1} region for laser-ablated Sc codeposited with 0.5% O_2 and 0.05% CCl_4 in argon. (a) Sample collected for 1 h at 10 K, (b) after annealing to 20 K, (c) after $\lambda > 470$ nm photolysis, (d) after full-arc photolysis, (e) after annealing to 30 K, and (f) after annealing to 35 K.

TABLE 1: Absorptions (cm^{-1}) Observed for Low-Power Laser-Ablated Scandium and O_2 Reaction Products in Solid Argon

$^{16}O_2$	$^{18}O_2$	$^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$	*R*(16/18)	assignment
1118.4	1055.8		1.0593	*trans*-O_4^-
1109.4	1046.8		1.0598	$(O_2)_xScO$
1106.8	1045.5		1.0586	$(O_2)_xScO$
976.3	935.5	976.3, 935.5	1.0436	ScO^+
954.8	915.1	954.8, 915.1	1.0434	ScO
953.7	901.6		1.0578	cyc-O_4^-
921.8	883.2	921.4, 883.6	1.0437	$(O_2)_xScO$
913.8	875.7	913.5, 876.0	1.0435	$(O_2)_xScO$
911.9	874.0	911.6, 874.3	1.0436	$(O_2)_xScO$
909.0	871.2	908.8, 871.3	1.0434	$(O_2)ScO$
892.9	850.4	892.9, 872.5, 850.4	1.0500	$Sc(O_2)^+$
818.6	773.8			ScO_3 site
804.0	759.2			ScO_3
733.3	706.8		1.0375	$OScO^-$ site
730.2				aggregrate
722.5	696.9	722.5, 704.9, 696.9	1.0367	$(OScO)^-$
641.1	614.4	641.1, 629.1, 614.4	1.0435	$Sc(O_2)^+$
624.8	593.6	624.8, 607.2, 593.6	1.0526	$Sc(O_2)^+$
552.6	536.2	547.7, 538.0, 529.5	1.0306	$Sc(O_2)_2$
466.3	451.2	466.3, 461.3, 451.2	1.0332	$(O_2)ScO$

increased the 976.3 cm^{-1} band and destroyed the weak 722.5 cm^{-1} band, as before, but increased the 892.9 cm^{-1} band 3 times, in contrast to the matrix without CCl_4. This behavior allowed two weaker bands at 641.1 and 624.8 cm^{-1} to be associated with the stronger 892.9 cm^{-1} band. Doping with CCl_4 had no effect on the 909.0−921.8 cm^{-1} bands.

Isotopic substitution shifted these bands, which are given in Table 1. In the $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ experiment, the 722.5 cm^{-1} band was previously shown to be an asymmetric 722.5, 704.9, 696.9 cm^{-1} triplet where the asymmetry in the position of the mixed isotopic component points to a higher frequency stretching mode for this species, which contains two equivalent oxygen atoms. The CCl_4 experiments gave a very weak triplet for this band with scrambled isotopic oxygen and a very weak 696.9 cm^{-1} counterpart in a separate $^{18}O_2$ experiment. The bands at 892.9, 641.1, and 624.8 cm^{-1} enhanced by CCl_4 gave triplet absorptions for a species with two equivalent oxygen atoms.

The low laser power and CCl_4 doping experiments clearly show that the 722.5 cm^{-1} band is due to an anion species, the 892.9, 641.1 and 624.8 cm^{-1} absorptions are due to a cation, and the 976.3 cm^{-1} band may also be due to a cation.

Theoretical Results and Discussion

Calculations were performed on many molecules and we include those that are relevant to the new experiments described above. In Table 2, we summarize our computed results for the ScO_2 species, while Tables 3 and 4 contains our results for O_2-ScO, ScO, ScO^+, and ScO^-.

The previous experimental work[1a] showed that the 722.5 cm^{-1} band arose from a species that had the formula ScO_2. Therefore our first series of calculations considered these species. This included ScO_2, ScO_2^+, and ScO_2^-, where the Sc has inserted into the O=O bond, and $Sc(O_2)^+$, where the Sc is bonded to the side of O_2. An inspection of Table 2 shows that ScO_2^- is the best match for the observed species. All of the theoretical approaches yield similar b_2 frequencies and isotopic ratios for ScO_2^-. We note the particularly good agreement of the isotopic ratios for the two highest levels of theory, CCSD(T) and CASPT2, with experiment. The difference between theory and

TABLE 2: Computed Harmonic Frequencies of ScO_2, ScO_2^+, ScO_2^-, and $Sc(O_2)^+$, in cm^{-1} ^{f}

	a_1	a_1	b_2	b_2 $R(16/18)$
ScO_2^-				
BP86	761(10)	183(27)	697(671)	
BP86/L	779(37)	209(53)	724(738)	1.0375
B3LYP	783(24)	188(68)	728(783)	
B3LYP/L	801(48)	208(83)	745(857)	1.0369
CCSD(T)	769	161	691	1.0365
CASPT2	724	66	682	1.0366
exptl			722.5	1.0367
$ScO_2^+(^3B_2)$				
BP86	596(38)	132(46)	462(35)	1.0377
BP86/L	598(42)	128(46)	464(37)	1.0380
B3LYP/L	699(51)	157(41)	707(100)	1.0389
CASPT2	824	132	750	1.0390
$ScO_2(^2B_2)$				
BP86^a	740(44)	116(55)	542(6)	
B3LYP/L	767(46)	131(73)	99(126)	
CCSD(T)^a	745^b	121	604	1.0362
CCSD(T)/B	742	122	615	
$ScO_2(^2A')$				
B3LYP^a	886(97)	133(51)	413(14)	
B3LYP/L	896(110)	131(60)	402(12)	
CASPT2	915^c	172	465	1.0455
$Sc(O_2)^+$				
BP86	932(57)^d	648(20)^e	623(27)	1.0541
exptl	892.9	641.1	624.8	1.0526

[a] Taken from reference 4. [b] Isotopic ratio is 1.0554. [c] Isotopic ratio is 1.0423. [d] Isotopic ratio is 1.0513; the experimental value is 1.0500. [e] Isotopic ratio is 1.0435; the experimental value is 1.0435. [f] The intensities are given in parentheses and are in km/mol. The b_2 mode oxygen isotopic ratio is also given

TABLE 3: BP86 Frequencies (cm^{-1}), Intensities (km/mol), and Isotopic Ratios for O_2ScO

O_2ScO						
frequency	159	160	426	454	907	1115
intensity	29	22	10	63	159	43
$R(16/18)$	1.0502	1.0508	1.0545	1.0333	1.0442	1.0607

TABLE 4: Frequencies (cm^{-1}), Intensities (km/mol), and Isotopic Ratios for the Diatomics

	BP86			CCSD(T)	
	frequency	intensity	$R(16/18)$	frequency	$R(16/18)$
ScO $^2\Sigma^+$	970	154	1.0438	973	1.0438
ScO^+ $^1\Sigma^+$	1039	127	1.0438	1023	1.0438
ScO^- $^1\Sigma^+$	910	138	1.0438	911	1.0438

experiment for the position of the b_2 band is more consistent with the expected accuracy of these methods than that of our previous assignment. As noted above, the new experiments confirm this assignment of the 722.5 cm^{-1} band to ScO_2^-.

The new experiments show that three bands (892.9, 641.1, and 624 cm^{-1}) are associated with the same molecule. Isotopic substitution suggests that it also has the formula ScO_2, and the CCl_4 experiments show that it is a cation. The results for the $^3B_2$ state of ScO_2^+ show that the frequencies for this molecule depend on the level of theory, as found previously for ScO_2. However the differences between methods are less dramatic for ScO_2^+. The B3LYP/L harmonic frequencies are in good agreement with the CASPT2 results, while the BP86 results differ significantly from the CASPT2 results. The B3LYP/L isotopic ratio is also in good agreement with the CASPT2 result. We do not see any experimental evidence for the formation of $OScO^+$ under our experimental conditions.

The most stable structure for the singlet state of ScO_2^+ is $Sc(O_2)^+$. The computed frequencies and isotopic ratios are good agreement with experiment, see Tables 1 and 2. Thus we assign the three bands at 892.9, 641.1, and 624 cm^{-1} to $Sc(O_2)^+$.

The bands at 954.8 and 976.3 cm^{-1} are assigned to ScO and ScO^+, respectively. While the differences between theory and experiment for the band positions are perhaps a bit larger than desired, theory and experiment are in good agreement for the isotopic ratios. The larger difference between theory and experiment for ScO^+ than for ScO is likely due to matrix effects, since the ion will interact more strongly with the matrix than the neutral. This is supported by the 29.8 cm^{-1} increase in the ScO^+ band when Ne is used instead of Ar, compared with the 7.9 cm^{-1} increase for ScO. ScO^- would have a similar isotopic ratio and the computed results show that its frequency is smaller than that of ScO. ScO^- photoelectron spectra[27] also show an anion vibrational frequency (840 cm^{-1}) smaller than that of the neutral. In addition, the CCl_4 experiment suggests that the 976.3 cm^{-1} band is due to a cation. We should note that at both CCSD(T) and BP86 levels, we find the ground state of ScO^- to be $^1\Sigma^+$, with the $^3\Delta$ which was previously assumed[27] to be the ground state, significantly higher (more than 9000 cm^{-1} at the CCSD(T) level) in energy.

As shown below, the best calculation for ScO_2 C_s predicts bands at about 915 and 465 cm^{-1}. While there are experimental bands in this region, namely, 909.0 cm^{-1}, the computed ScO_2 isotopic ratios differ significantly from the experimental values. Therefore other species were considered and the best match is obtained for $(O_2)ScO$, which also has a lower associated band at 466.3 cm^{-1}; compare the results in Tables 1 and 3. A series of related bands that we attribute to species with additional O_2 molecules coordinated to the O_2ScO species grow in on annealing along with the bands at 1109.4 and 1106.8 cm^{-1}. The computed O_2ScO results also support the assignment of the bands near 1100 cm^{-1} to this class of species.

Since the band at 722 cm^{-1} is now clearly assigned as the b_2 mode of ScO_2^-,the question arises, where are the ScO_2 bands? The experimental spectra were carefully analyzed and we find no bands that could obviously be assigned to ScO_2, even when the CCl_4 is used to minimize anion production. Therefore additional calculations were performed on ScO_2 to aid in the search for this molecule. These calculations reconfirm the problems associated with computing accurate frequencies for ScO_2. A detailed description of the new calculation on ScO_2 will be given elsewhere,[28] but here we wish to make a few comments relative to the search for the ScO_2 IR bands. Using the large basis set, we are able to find two solutions at the B3LYP level, one with C_{2v} symmetry and the second with C_s; see Table 2. The C_s results are similar to those obtained previously using the smaller basis set. While we are able to also find a solution with C_{2v} symmetry, the very low b_2 frequency suggests that this level of theory is not appropriate for this molecule. At the CASPT2 level, we are also able to find two solutions. The CASPT2 C_s solution yields harmonic frequencies similar to the B3LYP approach. The CASPT2 C_{2v} solution is about 5 kcal/mol below the C_s solution, but unfortunately the shape of the potential energy surface for the C_{2v} structure is so strange that we are unable to obtain frequencies.

We have repeated the CCSD(T) C_{2v} calculations using the “big” basis set and the results do not change significantly. In light of the CASPT2 results, C_s solutions were also explored. We find the CCSD(T) energy at the B3LYP C_s minimum to be 1.65 kcal/mol below the CCSD(T) C_{2v} minimum. However, when a symmetry broken SCF wave function (C_s symmetry) is used for the reference at the C_{2v} minimum, the symmetry broken

CCSD(T) result is 4.7 kcal/mol above the CCSD(T) C_{2v} solution. Ideally, at geometries with C_{2v} symmetry, there would be only one solution. The fact that we can find two solutions very close in energy at the C_{2v} geometry suggests that it is not possible to definitively determine the geometry of ScO_2 at the CCSD(T) level of theory. Bruekner doubles,[29] with a perturbational estimate of the triples, BD(T), has been used to study symmetry breaking problems,[30−31] and it would be very interesting to apply this approach to ScO_2. Unfortunately it is not practical for us to perform BD(T) calculations on ScO_2 using the same basis set as used in the CCSD(T) calculations with any of the programs that we have access to.

If we assume that the true system has C_{2v} symmetry, our best guess for the frequencies would be those obtained at the CCSD(T) level. Since the BP86 approach yields similar frequencies, we assume that the BP86 intensities are reliable. This would suggest that the a_1 mode at about 740 cm^{-1} would be the best chance to observe ScO_2. Using the ScO_2^- results to estimate the errors in the computed frequencies, we would expect ScO_2 to be observed near 770 cm^{-1} with an isotopic shift of 1.0554. We note that a weak band observed at 772.7 cm^{-1} in our first[1a] and current experiments could be OScO, but we cannot find an $^{18}O_2$ counterpart to support assignment. If the error in ScO_2 has the opposite sign as that found for ScO_2^-, it would fall in the same region as the b_2 band of ScO_2^- and hence might be hard to observe.

Photoelectron spectra[27] of ScO_2^- show a vibrational progress of 740 ± 80 cm^{-1}, which has been assigned to the a_1 mode of ScO_2. This would appear to support the C_{2v} structure of ScO_2. We note that the computed CCSD(T) and CASPT2 electron affinities of ScO_2 are 2.4 and 2.0 eV, respectively, which are in good agreement with the experimental value of 2.32 eV.

If the molecule really has C_s symmetry, the CASPT2 results would be our best estimate for the frequencies. Using ScO_2^- results to estimate the error and B3LYP/L for the intensities, we would expect the strongest ScO_2 band at 915 ± 40 cm^{-1}, with an isotopic ratio of 1.0423 and a weaker band at 465 ± 40 cm^{-1} with an isotopic ratio of 1.0455. As we noted above, we observe bands in these regions, but the isotopic ratios are inconsistent with ScO_2^-, and we have assigned them as O_2-ScO.

Conclusions

By adding CCl_4, an electron-trapping molecule, to the O_2 reagent, we have been able to determine the charge of some of the species giving rise to the observed IR bands. In addition, varying the conditions has allowed the observation of some weaker bands. Using these new experimental results and the results of new ab initio calculations, we have been able to assign several additional bands that arise from the products of the Sc reaction with dioxygen. We have reassigned the band at 722.5 cm^{-1} to ScO_2^-. We have assigned band at 976.2 cm^{-1} to ScO^+, those at 892.9, 641.1, and 624.8 cm^{-1} to $Sc(O_2)^+$, and those at 909.0 and 466.3 cm^{-1} to O_2ScO. The calculations also support assigning the bands at 1100 cm^{-1} to $(O_2)_xScO$ species. However, we are unable to assign any bands to ScO_2 nor are we able to make definitive predictions as to it vibrational frequencies.

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