

Isolated  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  Anions Do Not Exist

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Ab initio theoretical methods that incorporate effects of orbital relaxation and electron correlation are used to examine the possibility that doubly or triply charged oxy anions of the class  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ , or  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{SbO}_4^{3-}$  are stable relative to electron detachment in the absence of any surrounding medium. In all of these cases, our findings indicate quite clearly that these multiply charged oxy anions are *not stable*.

## Introduction

Multiply charged anions such as  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  play important roles in chemistry and biochemistry, where they appear as structural units of crystals, solutions, and molten substances. The bond lengths<sup>1</sup> and vibrational frequencies,<sup>2</sup> effective ionic radii, and electronic polarizabilities<sup>3</sup> as well as thermodynamic functions<sup>4</sup> of  $\text{SO}_4^{2-}$  and the bond lengths of  $\text{PO}_4^{3-}$ <sup>5</sup> have been determined experimentally. However, all of these data were obtained in some medium, which may act to stabilize and hence change the properties of the free anions. The question "Can these free anions exist?" is therefore still open.

The experimental results for free  $\text{SO}_4^{2-}$  are controversial. Kancerevicius<sup>6a</sup> and Schulten and Rollgen<sup>6b</sup> reported the observation of free  $\text{SO}_4^{2-}$  using field desorption mass spectrometry of inorganic ions from a polymeric matrix. However, several others' experimental studies<sup>7</sup> were not able to detect  $\text{SO}_4^{2-}$  in the gas phase. In theoretical work, Scheller and Cederbaum<sup>8d</sup> found that  $\text{CO}_3^-$  and a free electron are more stable than  $\text{CO}_3^{2-}$ , so free  $\text{CO}_3^{2-}$  does not exist. Recently, doubly charged anions such as  $\text{BeF}_4^{2-}$ ,<sup>8a</sup>  $\text{SeF}_8^{2-}$ ,  $\text{TeCl}_8^{2-}$ ,  $\text{TeF}_8^{2-}$ ,<sup>8b</sup> and  $\text{LX}_3^{2-}$  ( $\text{L} = \text{Li}, \text{Na}, \text{K}; \text{X} = \text{F}, \text{Cl}$ )<sup>8c,d</sup> have been studied using ab initio theoretical methods where it has been shown that, although all of these species are not stable thermodynamically with respect to loss of one  $\text{F}^-$ , they are geometrically metastable and electronically stable species with large dissociation barriers and hence large lifetimes.

## Methods Used

In this article we present results of our calculations for  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , and well as for the valence isoelectronic  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SbO}_4^{3-}$  ions. The bond lengths of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  were optimized by employing analytical gradients<sup>9</sup> using a polarized split-valence basis set (6-311+G\*)<sup>10</sup> at the MP2(full) level. The MP2 (full)/6-311+G\* equilibrium geometries were then used to evaluate electron correlation corrections in the frozen-core approximation by Møller–Plesset perturbation theory to full fourth order<sup>11</sup> and by the (U)QCISD(T) method<sup>12</sup> using 6-311+G\* basis sets. The UHF wave functions for open shell systems were projected to pure spectroscopic states, and the corresponding results are denoted PUHF, PMP2, PMP3, and PMP4.<sup>13</sup> Bond lengths for the isoelectronic  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SbO}_4^{3-}$  ions have been obtained using MP2 approximation and the Los Alamos pseudopotentials.<sup>14</sup> We used Dunning's valence double- $\zeta$  basis set (9s5p/3s2p) for the oxygen atoms<sup>15</sup> and valence 2s2p basis sets for the selenium, tellurium, arsenic, and antimony atoms<sup>14</sup> extended by polarization d-functions on all atoms and diffuse s- and p-functions on the oxygen atoms. Exponents for the polarization d-functions (0.293 (As), 0.338 (Se), 0.211 (Sb), 0.237 (Te)) were taken from ref 16, and exponents of the diffuse s- and p-functions 0.059 were taken from

ref 17. Finally, we calculated the total energies of  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{TeO}_4^{2-}$ , and the corresponding singly charged anions (with the detachment of one electron from the  $1t_1$ -HOMO and from the next lowest  $3t_2$ -HOMO-1) at the optimal geometry of the doubly charged anions at the MP $n$  ( $n = 2-4$ ), QCISD, and QCISD(T) levels and with the recently suggested Freenberg perturbation series (for details see ref 18 and references therein) FPT $n$  ( $n = 2-4$ ). The Gaussian 92 program suite<sup>19</sup> was used to perform all of the calculations whose results are discussed here.

## Results

Our optimal S–O bond length of 1.52 Å for isolated  $\text{SO}_4^{2-}$  is close to the corresponding values of 1.47–1.50 Å in various crystals, 1.50 Å in molten salts, and 1.50 Å in solutions. The orbital energy of the  $1t_1$ -HOMO is negative ( $\epsilon = -0.73$  eV), which means that this dianion is electronically stable within the Koopmans' theorem approximation. Taking orbital relaxation into account (i.e., carrying out separate SCF level calculations on  $\text{SO}_4^{2-}$  and  $\text{SO}_4^-$ ) in the so-called  $\Delta$ SCF treatment allows the total energy of  $\text{SO}_4^-$  to be found 1.10 eV lower than that of  $\text{SO}_4^{2-}$  at the optimal dianion geometry. Hence, the doubly charged anion is predicted to be electronically unstable at the  $\Delta$ SCF level. Because differential electron correlation energies can amount to 1 eV or more, it is therefore essential to examine the dianion and anion stabilities at various correlated levels. Doing so, we find that correlation corrections to the  $\Delta$ SCF prediction calculated at the PMP2, PMP3, PMP4, and QCISD(T) levels with 6-311+G\* basis sets *increase the instability* of  $\text{SO}_4^{2-}$  with respect to  $\text{SO}_4^-$  by approximately 0.2–0.4 eV. At our highest PMP4 and QCISD(T) levels, the dianion is less stable than the singly charged anion by 1.57 and 1.34 eV, respectively (see Table 1). Because the final state of the singly charged  $\text{SO}_4^-$  anion in the  $^2T_1$  electronic state is not geometrically stable at  $T_d$  symmetry due to Jahn–Teller distortion, the  $\text{SO}_4^-$  anion will be even more stable at its optimal geometry; therefore  $\text{SO}_4^{2-}$  is even more unstable with respect to electron detachment. Weikert and Cederbaum<sup>8e</sup> also have found that the  $\text{SO}_4^{2-}$  dianion is unstable to electron loss, according to the Green's function calculations.

The next occupied  $3t_2$ -(HOMO-1) orbital is more stable than  $1t_1$ -HOMO by 1.8 eV at Koopmans' approximation; however, due to a larger electron relaxation effect, at the  $\Delta$ SCF level, the energy difference between these two states is only 0.7 eV with the  $^2T_1$  electronic state lying lower. When electron correlation energy is taken into account, the  $^2T_1$  state of  $\text{SO}_4^-$  is only 0.2–0.4 eV lower than the  $^2T_2$  state at the optimal geometry for  $\text{SO}_4^{2-}$ . Calculated vertical detachment energies for both states at the FPT4 level are in the range of the corresponding values at the PMP4 and QCISD(T) levels. Because, at all correlated levels,  $\text{SO}_4^{2-}$  is not electronically stable, our final conclusion is that free

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TABLE 1: Calculated Vertical Electron Detachment Energies DE (eV)

species	MO	$\text{DE}_v^{\text{Koopmans}}$	$\text{DE}_v^{\text{ASCF}}$	$\text{DE}_v^{\text{PMP2}}$	$\text{DE}_v^{\text{PMP3}}$	$\text{DE}_v^{\text{PMP4}}$	$\text{DE}_v^{\text{QCISD}}$	$\text{DE}_v^{\text{QCISD(T)}}$
$\text{SO}_4^{2-}$	$1t_1$	+0.73	-1.10	-1.60	-1.13	-1.57	-1.10	-1.34
	$3t_2$	+2.54	-1.82	-0.96	-1.06	-1.19		
$\text{SeO}_4^{2-}$	$1t_1$	+1.55	-0.91	-0.82	-0.54	-0.88	-0.51	-0.72
	$3t_2$	+2.35	-1.47	-0.17	-0.23	-0.17		
$\text{TeO}_4^{2-}$	$1t_1$	+2.11	-0.47	-0.26	-0.03	-0.42	-0.12	-0.20
	$3t_2$	+2.40	-1.25	+0.55	+0.05	+0.21		
$\text{PO}_4^{3-}$	$1t_1$	-5.33		+0.09 <sup>a</sup>	+0.09 <sup>a</sup>	+0.10 <sup>a</sup>		
$\text{AsO}_4^{3-}$	$1t_1$	-4.33						
$\text{SbO}_4^{3-}$	$1t_1$	-3.52						

<sup>a</sup>  $\text{DE}_v$  calculated according to Feenberg perturbation theory series (see text).

$\text{SO}_4^{2-}$  does not exist as a stable species, which agrees with most of the available experimental data.<sup>7</sup> Our findings do not preclude the possibility that  $\text{SO}_4^{2-}$  can exist as a short-lived resonance state, but there exists in our data no hint of such behavior.

On the basis of previous calculations,<sup>20</sup> it is known that when the distances between the electronegative ligands in closed shell multiply charged anions increase, the stability of the HOMO increases also. Therefore, we expect the HOMOs of both  $\text{SeO}_4^{2-}$  and  $\text{TeO}_4^{2-}$  to be more stable than that of  $\text{SO}_4^{2-}$ , and perhaps one of these dianions can survive in the free state. Indeed, the orbital energies of the HOMOs vary in this manner:  $\text{SO}_4^{2-}$  (-0.73 eV),  $\text{SeO}_4^{2-}$  (-1.55 eV),  $\text{TeO}_4^{2-}$  (-2.11 eV). And at the Koopman's level both dianions are very stable with respect to electron loss.

The optimal bond length  $R(\text{Se}-\text{O}) = 1.678 \text{ \AA}$  of free  $\text{SeO}_4^{2-}$  is very close to the corresponding values in crystal salts:  $1.66 \pm 0.01 \text{ \AA}$  ( $(\text{NH}_4)_2\text{SO}_4^{21a}$ ),  $1.654 \pm 0.021 \text{ \AA}$  ( $\text{Na}_2\text{SeO}_4^{21b}$ ),  $1.65 \pm 0.01 \text{ \AA}$  ( $\text{K}_2\text{SeO}_4^{21c}$ ), and  $1.64 \text{ \AA}$  ( $\text{Rb}_2\text{SeO}_4^{21d}$ ). The corresponding Te crystal salts  $\text{Li}_2\text{TeO}_4^{22a}$  and  $\text{Na}_2\text{TeO}_4^{22b}$  are not composed of  $\text{TeO}_4^{2-}$  anions. Instead, the tellurium atoms occur in octahedral oxygen coordination in these salts. Our optimal bond length for  $\text{TeO}_4^{2-}$ ,  $R(\text{Te}-\text{O})$ , is equal to  $1.839 \text{ \AA}$ .

Both  $\text{SeO}_4^{2-}$  and  $\text{TeO}_4^{2-}$  have local minima at the tetrahedral structure because all of the computed vibrational frequencies are positive ( $\text{SeO}_4^{2-}$   $\nu_1(a_1) = 802 \text{ cm}^{-1}$ ,  $\nu_2(e) = 310 \text{ cm}^{-1}$ ,  $\nu_3(t_2) = 819 \text{ cm}^{-1}$ ,  $\nu_4(t_2) = 405 \text{ cm}^{-1}$ ;  $\text{TeO}_4^{2-}$   $\nu_1(a_1) = 738 \text{ cm}^{-1}$ ,  $\nu_2(e) = 250 \text{ cm}^{-1}$ ,  $\nu_3(t_2) = 744 \text{ cm}^{-1}$ ,  $\nu_4(t_2) = 318 \text{ cm}^{-1}$ . All at MP2). Therefore, if we keep the number of electrons constant, these dianions are geometrically stable. However, when electron relaxation and electron correlation are taken into account, both  $\text{SeO}_4^{2-}$  and  $\text{TeO}_4^{2-}$  are not electronically stable with respect to removal of an electron from the  $1t_1$ -HOMO to produce a  ${}^2T_1$  final electronic state (see Table 1). Therefore, we conclude that both of these free doubly charged anions do not exist either.

An important consequence of these calculations is that even if a multiply charged anion is very stable at the Koopman's approximation level (as happens for  $\text{TeO}_4^{2-}$ ), we should not trust these results. Electron relaxation and electron correlation are extremely important even for making qualitative predictions.

On the basis of results presented above for doubly charged anions, we did not expect that any of the triply charged  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SbO}_4^{3-}$  ions could survive even as metastable species. Our computational results confirm these predictions; all three anions have very positive HOMO energies:  $+5.33 \text{ eV}$  ( $\text{PO}_4^{3-}$ ),  $+4.33 \text{ eV}$  ( $\text{AsO}_4^{3-}$ ), and  $+3.52 \text{ eV}$  ( $\text{SbO}_4^{3-}$ ) at the corresponding optimal  $T_d(1A_1)$  geometries with bond lengths  $R(\text{P}-\text{O}) = 1.599 \text{ \AA}$ ,  $R(\text{As}-\text{O}) = 1.750 \text{ \AA}$ , and  $R(\text{Sb}-\text{O}) = 1.936 \text{ \AA}$ , calculated at the MP2/LANL1DZ+ $d_{\text{Te,O}}$ +diff.s. $_{\text{PO}}$  level. Not only is the HOMO energy positive, but the energies of a few other occupied orbitals are also positive. Therefore, these free triply charged anions are not electronically stable. Our findings do not preclude the possibility that  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ , and  $\text{TeO}_4^{2-}$  and triply  $\text{PO}_4^{3-}$ ,

$\text{AsO}_4^{3-}$ , and  $\text{SbO}_4^{3-}$  can exist as a short-lived resonance state, but there exists in our data no hint of such behavior.

The instability of the free doubly  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ , and  $\text{TeO}_4^{2-}$  and triply  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SbO}_4^{3-}$  charged ions studied here has important consequences. For example, in the thermochemical calculations of crystal energies for salts composed from these anions, one should not consider the anions as stable structural fragments, for the stable free fragment is actually the singly charged anion. Moreover, the structural parameters, harmonic frequencies, force constants, and other molecular properties for these doubly and triply charged anions should not be attributed not to the free anions but to anions in the crystal field that acts to stabilize the electronic state of the ion.

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