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by

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Isolated SO_4^{-2} and PO_4^{-3} Anions Do Not Exist

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Abstract

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 SO_4^{-2} , SeO_4^{-2} , TeO_4^{-2} , or PO_4^{-3} , AsO_4^{-3} , 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 oxyanions are not stable.

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I. Introduction

Multiply charged anions such as SO_4^{2-} and PO_4^{3-} play important roles in chemistry and biochemistry, where they appear as structural units of crystals, solutions and molten substances. The bond lengths¹ and vibrational frequencies², effective ionic radii and electronic polarizabilities³ as well as thermodynamic functions⁴ of SO_4^{2-} and the bond lengths of PO_4^{3-} ⁵ 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 SO_4^{2-} are controversial. Cancerevicius^{6a} and Schulten and Rollgen^{6b} reported observation free SO_4^{2-} using field desorption mass spectrometry of inorganic ions from a polymeric matrix. However, several others experimental studies⁷ were not able to detect SO_4^{2-} in the gas phase. In theoretical work, Scheller and Cederbaum^{8d} found that CO_3^- and a free electron are more stable than CO_3^{2-} , so free CO_3^{2-} does not exist. Recently, doubly charged anions such as BeF_4^{2-} ,^{8a} SeF_8^{2-} , TeCl_8^{2-} , TeF_8^{2-} ,^{8b} LX_3^{2-} ($\text{L}=\text{Li}, \text{Na}, \text{K}$; $\text{X}=\text{F}, \text{Cl}$)^{8c,d} 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 F^- , they are geometrically metastable and electronically stable species with large dissociation barriers and hence large lifetimes.

II. Methods Used

In this article we present results of our calculations for SO_4^{2-} and PO_4^{3-} , as well as for the valence isoelectronic SeO_4^{2-} , TeO_4^{2-} , AsO_4^{3-} and SbO_4^{3-} .

ions. The bond lengths of SO_4^{-2} and PO_4^{-3} were optimized by employing analytical gradients⁹ using a polarized split-valence basis set (6-311+G*)¹⁰ at the MP2(full) level. The MP2 (full)/6-31+G* equilibrium geometries were then used to evaluate electron correlation corrections in the frozen-core approximation by Møller-Plesset perturbation theory to full fourth order¹¹ and by the (U)QCISD(T) method¹² 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 PMP4.¹³ Bond lengths for the isoelectronic SeO_4^{-2} , TeO_4^{-2} , AsO_4^{-3} and SbO_4^{-3} have been obtained using the MP2 approximation and the Los Alamos pseudopotentials.¹⁴ We used Dunning's valence double-zeta basis set (9s5p/3s2p) for the oxygen atoms¹⁵ and valence 2s2p basis sets for the selenium, tellurium, arsenic and antimony atoms¹⁴ 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 SO_4^{-2} , SeO_4^{-2} , 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 MPn (n=2-4), QCISD, QCISD(T) levels and using the recently suggested Feenberg perturbation series (For details see Ref. 18 and references therein) FPTn (n=2-4). The Gaussian 92 program suite¹⁹ was used to perform all of the calculations whose results are discussed here.

III. Results

Our optimal S-O bond length 1.52 Å for isolated SO_4^{2-} is close to the corresponding values 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. Because the Koopmans' level description involves doubly occupied molecular orbitals, it is unable to describe electron ejection to $\text{SO}_4^- + e^-$. By taking orbital relaxation into account (i.e., carrying out separate SCF level calculations on SO_4^{2-} and SO_4^-) in the so-called Δ SCF treatment, the total energy of SO_4^- is found to be 1.10 eV lower than SO_4^{2-} at the optimal dianion geometry. Hence, the doubly charged anion is predicted to be electronically unstable at the Δ 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 Δ SCF prediction calculated at the PMP2, PMP3, PMP4 and QCISD(T) levels with 6-311+G* basis sets increase the instability of SO_4^{2-} with respect to 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 eV and 1.34 eV, respectively (see Table 1). Because the final state of the singly charged SO_4^- anion in the 2T_1 electronic state is not geometrically stable at T_d symmetry due to Jahn-Teller distortion, the SO_4^- anion will be even more stable at its optimal geometry, therefore SO_4^{2-} is even more unstable with respect to electron detachment. Weikert and Cederbaum^{8e} also have found that 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 Δ 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 SO_4^- is only 0.2-0.4 eV lower than the 2T_2 state at the optimal geometry for 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, SO_4^{2-} is not electronically stable, our final conclusion is that free SO_4^{2-} does not exist as a stable species, which agrees with most of the available experimental data.⁷ Our findings do not preclude the possibility that SO_4^{2-} can exist as a short-lived resonance state, but there exists in our data no hint of such behavior.

Based on previous calculations,²⁰ 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 SeO_4^{2-} and TeO_4^{2-} to be more stable than that of SO_4^{2-} and perhaps one of these dianions can survive in the free state. Indeed, the orbital energies of the HOMOs varies in this manner: SO_4^{2-} (-0.73 eV), SeO_4^{2-} (-1.55 eV), 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 $R(\text{Se-O})=1.678 \text{ \AA}$ of free SeO_4^{2-} is very close to the corresponding values in crystal salts: $1.66\pm0.01 \text{ \AA}$ ($(\text{NH}_4)_2\text{SO}_4^{21a}$), $1.654\pm0.021 \text{ \AA}$ ($\text{Na}_2\text{SeO}_4^{21b}$), $1.65\pm0.01 \text{ \AA}$ ($\text{K}_2\text{SeO}_4^{21c}$) 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 TeO_4^{2-} anions. Instead, the tellurium atoms occur in

octahedral oxygen coordination in these salts. Our optimal bond length for TeO_4^{2-} $R(\text{Te-O})$ is equal to 1.839 Å.

Both SeO_4^{2-} and TeO_4^{2-} have local minima at the tetrahedral structure because all of the computed vibrational frequencies are positive (SeO_4^{2-} : $\nu_1(a_1)=802\text{ cm}^{-1}$, $\nu_2(e)=310\text{ cm}^{-1}$, $\nu_3(t_2)=819\text{ cm}^{-1}$, $\nu_4(t_2)=405\text{ cm}^{-1}$ and 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 SeO_4^{2-} and 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 Koopmans' approximation level (as happens for TeO_4^{2-}), we should not trust these results. Electron relaxation and electron correlation are extremely important even for making qualitative predictions.

Based on the results presented above for doubly charged anions, we did not expect that any of the triply charged PO_4^{3-} , AsO_4^{3-} and 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 eV (PO_4^{3-}), +4.33 eV (AsO_4^{3-}) and +3.52 eV (SbO_4^{3-}) at the corresponding optimal $T_d(^1A_1)$ geometries with bond lengths $R(\text{P-O})=1.599\text{ Å}$, $R(\text{As-O})=1.750\text{ Å}$ and $R(\text{Sb-O})=1.936\text{ Å}$, calculated at the MP2/LANL1DZ+ $d_{\text{Te,O}}+\text{diff.s,p}_O$ 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 SO_4^{2-} ,

SeO_4^{-2} , TeO_4^{-2} and triply PO_4^{-3} , AsO_4^{-3} , 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 SO_4^{-2} , SeO_4^{-2} , TeO_4^{-2} and triply PO_4^{-3} , AsO_4^{-3} , SbO_4^{-3} charged studied here has important consequences. For example, in the thermochemic calculations of crystal energies for salts composed from these anions, one should not consider the anions as stable structural fragments, 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 to the free anions, but to anions in the a crystal field that acts to stability the electronic state of the ion.

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Table 1. Calculated vertical electron detachment energies DE (eV).

Species	MO	DE _V ^{Koopmans}	DE _V ^{ΔSCF}	DE _V ^{PMP2}	DE _V ^{PMP3}	DE _V ^{PMP4}	DE _V ^{QCISD}	DE _V ^{QCISD(T)}
SO ₄ ²⁻	1t ₁	+0.73	-1.10	-1.60	-1.13	-1.57	-1.10	-1.34
				-1.17a	-1.17a	-1.43a		
	3t ₂	+2.54	-1.82	-0.96	-1.06	-1.19		
SeO ₄ ²⁻				-1.05a	-1.05a	-1.19a		
	1t ₁	+1.55	-0.91	-0.82	-0.54	-0.88	-0.51	-0.72
				-0.56a	-0.56a	-0.78a		
TeO ₄ ²⁻	3t ₂	+2.35	-1.47	-0.17	-0.23	-0.17	-0.76	-0.48
				-0.21a	-0.21a	-0.36a		
	1t ₁	+2.11	-0.47	-0.26	-0.03	-0.42	-0.12	-0.20
PO ₄ ³⁻				-0.06a	-0.06a	-0.31a		
	3t ₂	+2.40	-1.25	+0.55	+0.05	+0.21		
				+0.09a	+0.09a	+0.10a		
AsO ₄ ³⁻	1t ₁	-5.33						
SbO ₄ ³⁻	1t ₁	-4.33						
	1t ₁	-3.52						

^a DE_V calculated according to Feenberg perturbation theory series (see text).