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Stabilization calculation of the energy and lifetime of metastable SO_4^{2-}

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It is known that SO_4^{2-} is not electronically stable as an isolated species but can be rendered stable by solvation (e.g., by adding a few H_2O molecules). Recently, our group introduced a Coulomb repulsion model that offers an approximation to the energy instability and lifetimes of such species. In order to achieve an independent and likely more reliable estimate of the instability of SO_4^{2-}, we have undertaken a follow-up study of this dianion. Specifically, we apply a stabilization method to determine the vertical electronic energy difference between the metastable SO_4^{2-} dianion and its SO_4^{-1} daughter at several levels of theory. The particular variant of the stabilization method used here involves adding a partial positive charge to the central sulfur nucleus in order to confine the escaping electron. Our coupled-cluster data, which represent our highest level of theory, suggest that SO_4^{2-} is unstable by 1.1 eV and has a lifetime with respect to electron loss of 1.6×10^{-10} s (our earlier estimates were 0.75 eV and 2.7×10^{-8} s).
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I. INTRODUCTION

It is known[1] that isolated SO_4^{2-} is not electronically stable. This dianion, solvated by a few H_2O molecules, has been the subject of recent experimental studies[2] and remains the subject of much interest. In an earlier effort[3] we approximated the vertical energy difference between the metastable dianion SO_4^{2-} and its singly charged daughter SO_4^- using what we called a repulsive Coulomb model. We applied the model to a variety of dianions known to be electronically stable and found it to yield reasonable estimates of their electron binding energies. We were therefore encouraged to extend the model's applications to metastable species and we thus estimated the SO_4^{2-} to SO_4^- energy gap by:

(i) computing, at the same frozen geometry used for SO_4^{2-}, the SO_4^- to SO_4 neutral energy difference Δ, and then reducing Δ by an amount C that
(ii) represents the Coulomb repulsion between the two excess charges in SO_4^{2-} that is not present in SO_4^-.

The anion-neutral energy difference is taken as a measure of the intrinsic electron binding energy of each of the oxygen-based orbitals. The dianion-anion energy gap is then approximated as this intrinsic difference reduced by the Coulomb repulsion $C=e^2/R_{LL}$ between the two electrons in orbitals on two oxygen ligands a distance R_{LL} apart.

This model assumes that the two electrons removed from SO_4^{2-} to form SO_4^- and from SO_4^- to produce SO_4 reside in orbitals localized on the oxygen "ligands." It also requires that the eight nonbonding ligand molecular orbitals (of e, t_2, and t_1 symmetry comprised of oxygen $2p_\pi$ orbitals) are (essentially) degenerate. This degeneracy allows one to show that a Slater determinant in which a hole occurs in one of these symmetry-adapted molecular orbitals has the same energy as a determinant with a hole in a ligand-localized oxygen $2p_\pi$ orbital. This, in turn, allows one to evaluate the Coulomb repulsion component of the dianion-anion energy gap in terms of ligand–ligand repulsion energies (rather than in terms of symmetry- orbital Coulomb integrals).

However, for SO_4^{2-} the e, t_2, and t_1 orbitals are not degenerate (i.e., they have energies of -0.12, -0.09, and -0.03 Hartrees, respectively), so the difference between the t_1 HOMO energy (-0.85 eV) and the average of the three t_1, three t_2, and two e orbital energies (-2.0 eV) is substantial. Since the applicability of the Coulomb model to SO_4^{2-} is questionable, alternative methods for examining this dianion were used. As noted earlier, the Coulomb model was demonstrated in Ref. 3 to yield reliable predictions when applied to electronically stable dianion-anion-neutral species (e.g., MgF_4^{2-}, TeF_8^{2-}, BeF_4^{2-}) whose energies could be computed independently. However, for these species the energy splittings among the symmetry-adapted molecular orbitals derived from the ligand-localized orbitals were significantly smaller than for SO_4^{2-}. Finally, the Coulomb model was also shown to produce predictions[3] for dianion-anion energy gaps and lifetimes for metastable dianions (e.g., CO_3^{2-}, $PtCl_4^{2-}$) that are in reasonable agreement with what had been obtained by other workers[4–6] and by us using alternative techniques.[3]

In the present paper, we return to the SO_4^{2-} case, which is of significant current experimental interest,[2] and attempt to determine both the energy of SO_4^{2-} relative to SO_4^- and the lifetime of this dianion using a stabilization-based method[7] rather than the repulsive Coulomb model. We again emphasize that we undertook these calculations in order to obtain an independent determination of SO_4^{2-}'s energy and lifetime using a widely used method. The stabilization technique is well-established[7] and has been tested on a variety of metastable species. Thus, its application is likely to provide at least as reliable a prediction as that obtained using the Coulomb model.

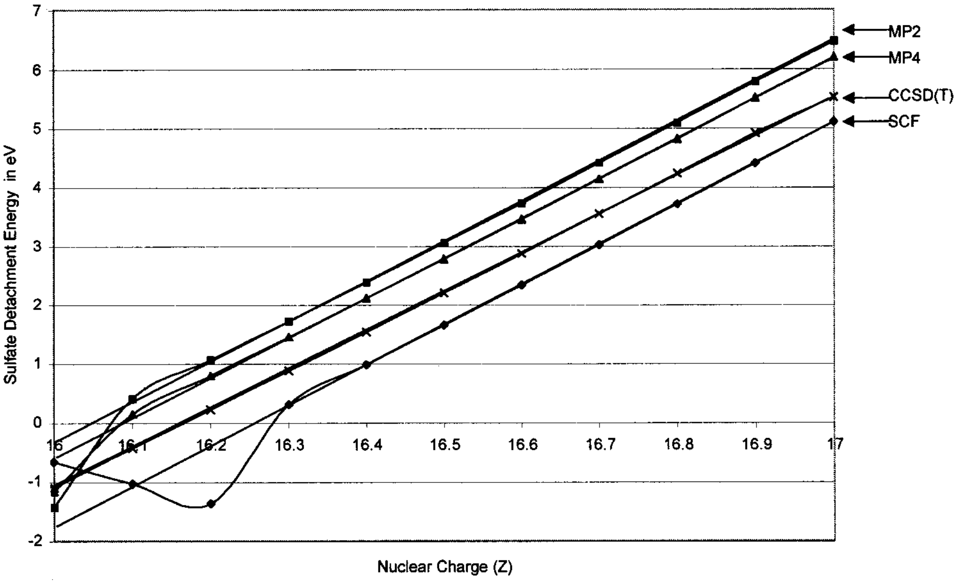

FIG. 1. Plot of detachment energy vs nuclear charge computed at various levels of theory. Linear fits to data with positive detachment energies are also shown and extrapolated.

II. METHODS

All the calculations of electron binding energies were performed with aug-cc-pVDZ basis sets.[8] Additional extra-diffuse basis functions were not included because the stabilization potential used to treat the metastable SO$_4^{2-}$ causes the charge density to be spatially compact. Although we examined the possibility that removing an electron from one of the e or t_2 orbitals would produce a lower energy for SO$_4^{-1}$, we found the $^2T_1$ state to be lower, so it is this state for which we report data below. The spin contamination of the $^2T_1$ SO$_4^{-1}$ monoanion remained small with $\langle S^2 \rangle$ values near 0.77 for values of the stabilizing potential (see below) used to extrapolate and determine the SO$_4^{2-}$ energy and lifetime. Because SO$_4^{-1}$ has five electrons in its t_1 orbitals, the SCF calculations on it display symmetry breaking (i.e., the three t_1 orbitals do not have identical LCAO-MO coefficients). However, this symmetry breaking is small and found to be especially small for sulfur nuclear charges Z (see below) greater than 16.3. Because we obtain our final predictions by extrapolation from this range of Z values, we believe that the level of symmetry breaking is benign. All calculations were performed with the GAUSSIAN98 program[9] on our Pentium III 450 MHz and AMD 950 MHz computers, and the three-dimensional plots of the molecular orbitals were generated with the MOLDEN program.[10]

After determining the optimal geometry of the closed-shell ground state SO$_4^{2-}$ at the MP2 level of theory ($R_{\mathrm{so}} = 2.53$ Å), we carried out a series of SO$_4^{2-} \rightarrow$ SO$_4^{-}$ electron binding energy calculations at a variety of levels ranging from Koopmans' theorem[11] to coupled-cluster singles and doubles including perturbative triples corrections[12] [CCSD(T)]. As discussed earlier, we obtain the ground state of SO$_4^{-1}$ by removing an electron from one of the three degenerate t_1 HOMOs of SO$_4^{2-}$. Because SO$_4^{2-}$ is not electronically stable with respect to electron loss to generate SO$_4^{-}$, it is not rigorously appropriate to compute its electronic energy by simply performing an SCF, MPn or CCSD(T) calculation. Specifically, if a much more flexible atomic orbital basis set were used, the SCF process (carried out in the UHF manner) would produce an energy for SO$_4^{2-}$ equal to that of SO$_4^{-}$ and a wave function equal to the UHF function of SO$_4^{-}$ multiplied by a free-electron function having zero kinetic energy. That is, the UHF process would undergo variational collapse. Because the SCF orbitals and energies form the starting point for the MPn and CCSD(T) calculations, this problem also plagues the latter methods. It is for this reason that we must use the stabilization method, which allows us to compute the energy of SO$_4^{-2}$ as if it were electronically stable and to subsequently extrapolate such data into the range of interest where SO$_4^{2-}$ is unstable.

In the present work, we introduce the stabilization tool as follows:

(1) We first calculate the electron binding energy of sulfate but using a sulfur nuclear charge (Z) of 17.0, in effect adding a stabilizing unit positive charge to the sulfur nucleus. This makes our system equivalent to a chlorate anion (which is known to be electronically stable) but with the sulfate dianion's MP2 geometry. As noted above, we compute the binding energy at a variety of levels ranging from Koopmans' theorem to CCSD(T).

(2) Next, we calculate the binding energy at sulfur nuclear charges of $Z = 16.9$, 16.8, etc., down to the standard sulfur charge $Z = 16.0$. A plot of the resultant electron detachment energy (DE) vs Z is shown in Fig. 1. Note that the data are linear when plotted as DE vs Z whenever the binding energy is positive (i.e., when the dianion is electronically stable) but the data deviate significantly from linearity when DE becomes negative. This observation reflects the electronic instability pathology discussed earlier when we explained why the stabilization technique is needed.

(3) To obtain our estimate of the energy of SO$_4^{2-}$ relative to SO$_4^{-}$, we extrapolate the linear regions of the plots of DE vs Z down to $Z = 16.0$. In a more speculative venture, we also extrapolate these linear plots to $Z = 15.0$ to

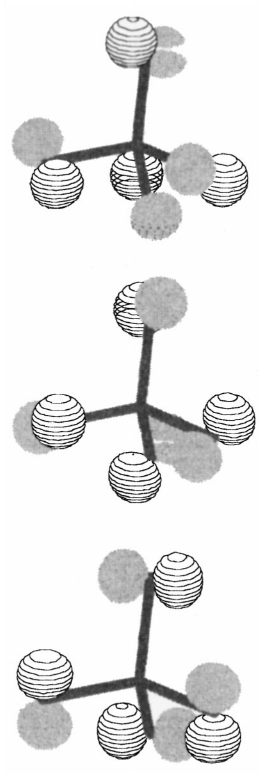

FIG. 2. Degenerate t_1 HOMOs of SO_4^{2-} showing their strong oxygen ligand localization.

obtain an estimate of the instability of the phosphate trianion which we also examined in Ref. 3 with our Coulomb model.

We should note that the approach we used is not a conventional application of the stabilization method. More typically[7] one would compute the energies of many electronic states of SO_4^{2-} using a variety of diffuse basis sets. For example, one might scale the orbital exponents of the more diffuse oxygen-centered basis orbitals by an amount η and then plot the energies of the various SO_4^{2-} states computed, for example, in a configuration interaction calculation, versus η. By searching for energies that remain relatively stable over significant ranges of η, one can identify candidates for metastable states. In the present study, we replace the scaling of the orbital exponents, which is designed to vary the radial extent of the metastable orbital, by the variable nuclear charge on sulfur, which serves a similar purpose. We chose this approach because we believe it offers a more efficient mechanism for addressing the problem at hand.

After calculating the energy of the metastable state, we use a one-dimensional tunneling model[3,13] to calculate the lifetime of sulfate with respect to electron loss. We also estimated the lifetime for phosphate using this same technique. In Ref. 13 this tunneling model was shown to be reliable, and its sensitivity to the functional form of the potential was examined. Moreover, in Ref. 3, we examined different forms for the radial potential to determine how the computed lifetimes varied. For example, in both Refs. 3 and 13, a potential was computed by evaluating the energy of the SO_4^{-1} anion in the presence of a unit negative charge (i.e., the ejected electron) at various distances (r) and at an orientation chosen to produce the lowest barrier (and thus the most facile tunneling). The resulting potential displays the proper 1/r Coulomb form at large-r, but its small-r behavior was somewhat different from that shown (see Fig. 3). For example, the Coulomb model potential used here has a barrier of 5.88 eV, whereas the test-charge derived model had a barrier of 4.37 eV. Nevertheless, a primary conclusion of that study for SO_4^{2-} was that the computed lifetime varies by less than one order of magnitude for this kind of variation in the potential.

TABLE I. Electron binding energies (eV) and lifetimes (s) of SO_4^{2-} and PO_4^{-3} at various levels of theory.

Sulfate	SCF	KT	CCSD(T)	Phosphate
Energy	-1.76	-0.85	-1.12	-7.80
Lifetime	2.04×10^{-12}	1.88×10^{-8}	1.63×10^{-10}	1.23×10^{-14}

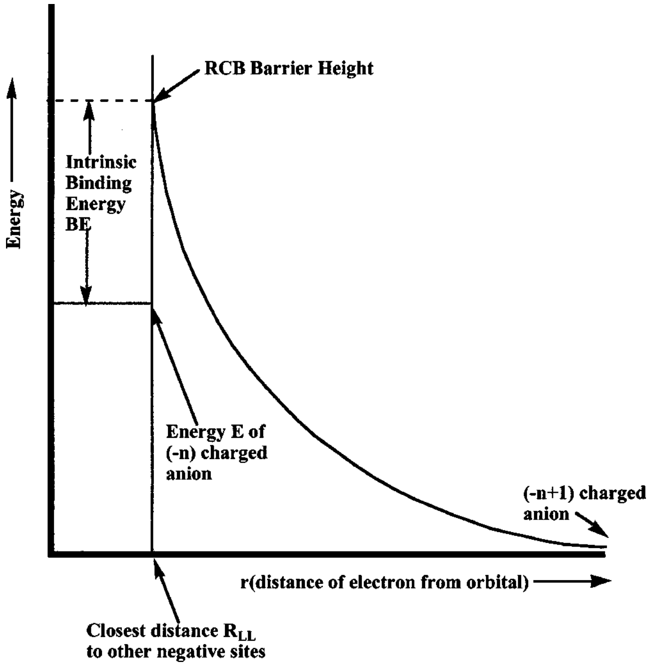

FIG. 3. One-dimensional model potential for calculating tunneling lifetimes.

III. RESULTS AND SUMMARY

As shown in Fig. 2, the t_1 HOMO orbitals of SO_4^{2-} are localized on the oxygen ligands. However, as noted earlier, their orbital energies (-0.85 eV) differ substantially from those of the t_2 (-2.4 eV) and e (-3.2 eV) orbitals which are comprised of the same eight oxygen $2p_\pi$ orbitals. For the latter reason, it was by no means clear that the Coulomb model used earlier[3] should be expected to produce relatively reliable predictions. In Table I, we summarize the energies determined by extrapolating our stabilization calculations. In particular, the detachment energies extrapolated to $Z=16$ give us the predicted instabilities of the SO_4^{2-} dianion, with our most accurate estimate being 1.12 eV [at the CCSD(T) level]. The corresponding tunneling lifetime, obtained using the one-dimensional potential[13] shown in Fig. 3 and discussed in Ref. 3 is 1.6×10^{-10} s. In our earlier Coulomb model calculations, we obtained an instability of 0.75 eV and a lifetime of 2.7×10^{-8} s. So, our stabilization results suggest a more unstable and shorter-lived SO_4^{2-} than we earlier predicted. Because the atomic basis sets and levels of theory [i.e., CCSD(T)] used in Ref. 3 and in the present work are the same, the differences in computed energies and lifetimes result from differences between the Coulomb model and the stabilization method. Because the latter is well tested on a variety of problems, we conclude that more realistic estimates for SO_4^{2-} are those obtained in the present study.

It should be noted, as clearly shown in Fig. 1, that we obtain a significant range of values for the instability energy of SO_4^{2-} at various levels of theory. Our Koopmans' theorem result is -0.85 eV, and our best prediction is -1.12 eV; however, intermediate levels of theory produce data ranging from -1.7 eV (SCF) to -0.4 eV (MP2). Therefore, we cannot claim that results obtained with the conventional systematic series of approximations [e.g., KT, SCF, MP2, MP4, CCSD(T)] have converged. Moreover, the computed tunneling lifetimes depend exponentially upon the energy difference between the top of the barrier (see Fig. 3) and the energy of the metastable state. As a result, the lifetimes computed for the rather wide range of energies noted above span a wide range. Nevertheless, we believe that the CCSD(T) energy and lifetime presented in this work offer the most reliable data currently available to the scientific community. We do not foresee how qualitatively better data could be obtained with currently available theory (e.g., with increased basis set size or using alternative correlation methods).

When we extrapolate our CCSD(T) data to $Z=15$, we are able to predict the instability of the PO_4^{3-} trianion. Doing so, we obtain an instability energy of 7.8 eV, and, again using the one-dimensional tunneling potential, we then compute a lifetime of 1.2×10^{-14} s. In Ref. 3, we suggested that PO_4^{3-} is unstable by 5.7 eV and has a lifetime of 9.4×10^{-14} s.

In summary, although it was earlier emphasized that isolated SO_4^{2-} is not electronically stable, the energy and lifetime of this species have not yet been examined using a variety of theoretical methods. Because these parameters have not yet been determined experimentally, it is prudent to study them with all means currently available. Earlier, we used a Coulomb repulsion-based model to estimate the energy and a radial tunneling model to approximate the lifetime. In the present work, we applied a more widely used and successful tool, the stabilization method, to gain another (presumably more reliable) estimate of the energy. Thus, we suggest, on the basis of our *ab initio* stabilization-based calculations performed at the CCSD(T) level, that:

(1) SO_4^{2-} is vertically electronically unstable by 1.12 eV.
(2) SO_4^{2-} has a lifetime with respect to electron detachment of 1.6×10^{-10} s.
(3) A crude extrapolation to the PO_4^{3-} case (but at the geometry of SO_4^{2-}) gives an energy instability of 7.8 eV and a lifetime of 1.2×10^{-14} s.
(4) The range of energies obtained at various levels of theory is significant, thus limiting our ultimate confidence limits on our final energy and lifetime predictions. The value reported above results from our highest level CCSD(T) treatment.

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