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Ab Initio Probing of the Aromatic Oxygen Cluster O_4^{2+}

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The structure of the O_4^{2+} dication has been studied theoretically using a few conventional theoretical methods. We found the O_4^{2+} dication to be a metastable species with a perfect square structure. The molecular orbital analysis reveals that this dication is the first all-oxygen aromatic system with 6π electrons. Although the O_4^{2+} dication is highly thermodynamically unstable, we believe that appropriate counteranions with very high electron detachment energy (superhalogens) can be found to form a solid-state compound containing O_4^{2+}. Another way to probe the planar aromatic tetra oxygen dication could be a double-photoionization process of the $(O_2)_2$ dimer.

1. Introduction

To date, there are only molecules known, which have three covalently bound oxygen atoms. Although covalently bound tetraatomic neutral oxygen species have been theoretically predicted, such as the bound cyclic (D_{2h}) of Adamantidies et al.[1] or the D_{3h} form analogous to SO_3,[2,3] these structures were found to be highly unstable lying ∼5.3 and ∼6.5 eV higher in energy, respectively, than two separate O_2 molecules. Indeed, the predicted covalent O_4 structures have still not been experimentally observed.[4] The $M^+O_4^-$ (M = Na, K, Rb, and Cs) molecules and the isolated O_4^- anion have been studied extensively via matrix isolation works (see ref 5 and references therein). Quantum chemical calculations by Chertihin and Andrews agreed well with observed infrared spectra of the O_4^- anion in Ar matrixes, showing that O_4^- has a rectangular structure with two short O−O distances (1.267 Å) and two long O−O distances (2.073 Å). Gas-phase mass spectrometric studies[6,7] revealed the anion to be stable with respect to O_2 + O_2^- by about 0.46 eV. Its photoelectron spectra were reported by Hanold and Continetti.[8] The highly accurate ab initio calculations of Aquino et al.[9] on O_4^- have given results in good agreement with the infrared spectra of O_4^- in Ar matrixes[5] and the photodissociation and photodetachment data.[8]

We recently proposed[10] that two oxygen dianions, O_4^{2-} and O_5^{2-}, valence isoelectronic to ClO_3^- and SO_3^{2-} and to ClO_4^- and SO_4^{2-}, respectively, could be a part of MO_4^- and MO_5^- ions. However, experimental spectra[10] did not produce convincing proof that covalently bound oxygen O_4^{2-} and O_5^{2-} dianions were actually assembled in molecular beams containing MO_4^- and MO_5^- ions. We also probed whether ozonic acid, H_2O_4 (isostructural to a sulforius acid) and its ionic salt Li_2O_4 and Na_2O_4 molecules could be stable.[11] We found that the ozonic acid H_2O_4 most probably is not stable and our results were inconclusive for salt Li_2O_4 and Na_2O_4 molecules. We still have a hope that such salts can be stabilized in the solid state by the addition of the Madelung field. We have shown[11] that a specially designed FLi_3O_4 molecule containing the pyramidal O_4^{2-} dianion (isostructural to SO_3^{2-}) is a stable species, against all gas-phase dissociation channels, containing the O_4^{2-} dianion, allowing the possibility for synthesis of materials with covalently bound tetraatomic oxygen atoms.

In this article, we probe another charged tetraatomic oxygen cluster, the aromatic O_4^{2+} cation. We were not able to find in the literature any publication on O_4^{2+}, even though the valence isoelectronic doubly charged cations S_4^{2+}, Se_4^{2+}, and Te_4^{2+}, are well characterized experimentally[12−23] and theoretically.[24−32] There are also review articles on these dications.[33−36] Our calculations of the O_4^{2+} dication shown that the planar square structure is a true minimum on the potential energy surface with equilibrium bond length and harmonic frequencies being in the expected range. We therefore believe that there is hope for making a compound with the O_4^{2+} dication.

2. Theoretical Method

An accurate theoretical treatment of metastable multiply charged species requires solution of the time-dependent Schrodinger equation. However, it was shown for S_4^{2+} and Se_4^{2+} [24−32] that conventional approximations for the time-independent Schrodinger equation could provide a reasonable description of these species, because they correspond to local minima separated by a barrier from dissociation. We, therefore, will also use conventional ab initio methods in describing properties of the O_4^{2+}, as well as S_4^{2+} and Se_4^{2+} dications. We optimized geometries and calculated harmonic frequencies of O_4^{2+}, S_4^{2+}, and Se_4^{2+} using two theoretical methods: B3LYP[37−39] and CCSD(T)[40−42] with the 6-311+G* basis sets.[43−46] The energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311+G(2df) basis sets. In order test the applicability of the one-electron configuration, we also ran RHF/6-311+G* and complete active space self-consistent field method[47,48] with 8 active electrons and 8 active molecular orbitals (CASSCF(8,8)/6-311+G*) calculations for O_4^{2+}. Since, for O_4^{2+} species, the CASSCF calculation did not agree well with the other correlation methods, we ran a CASSCF with the same active space coupled to a multireference configuration interaction, CASSCF(8,8)-MRCISD,[49,50] calculation. The same basis sets, 6-311+G*, were used. Aromaticity in the dications was probed through the calculations of the nucleus-independent chemical shift (NICS) indices proposed by Schleyer and co-workers.[51] All calculations were performed using the Gaussian 03[52] program, except for the CASSCF-MRCISD, which was performed using the MOLPRO 1999.[53]

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TABLE 1: Calculated and Experimental Molecular Parameters of O_4^{2+}, S_4^{2+}, and Se_4^{2+}

O_4^{2+}	E_{tot}, a. u.	R(O−O), Å	$\omega_1(a_{1g})$, cm^{-1}	$\omega_2(b_{1g})$, cm^{-1}	$\omega_3(b_{2g})$, cm^{-1}	$\omega_4(b_{2u})$, cm^{-1}	$\omega_5(e_u)$, cm^{-1}
B3LYP/6-311+G*	−299.39436	1.357	1068	1112	1220	590	804
RHF/6-311+G*	−297.87330	1.263	1503	1481	1633	753	996
CASSCF(8,8)/6-311+G*	−297.99879	1.282	1304	1293	1445	660	1122
CCSD(T)/6-311+G*	−298.79525	1.383	916	1011	1073	534	531

S_4^{2+}	E_{tot}, a. u.	R(S−S), Å	$\omega_1(a_{1g})$, cm^{-1}	$\omega_2(b_{1g})$, cm^{-1}	$\omega_3(b_{2g})$, cm^{-1}	$\omega_4(b_{2u})$, cm^{-1}	$\omega_5(e_u)$, cm^{-1}
B3LYP/6-311+G*	−1591.99276	2.072	521	343	569	201	464
CASSCF(8,8)/6-311+G*	−1589.31852	2.033	588	386	638	203	458
CCSD(T)/6-311+G*	−1589.86267	2.071	506	333	557	186	457
experiment[a]		2.011(3)	587 ± 3	374 ± 7	606 ± 3		

Se_4^{2+}	E_{tot}, a. u.	R(Se−Se), Å	$\omega_1(a_{1g})$, cm^{-1}	$\omega_2(b_{1g})$, cm^{-1}	$\omega_3(b_{2g})$, cm^{-1}	$\omega_4(b_{2u})$, cm^{-1}	$\omega_5(e_u)$, cm^{-1}
B3LYP/6-311+G*	−9605.47559	2.343	307	172	325	108	280
CCSD(T)/6-311+G*	−9599.01762	2.359	293	161	312	98	269
experiment[a]		2.284(4)	324 ± 3	185 ± 3			303 ± 4

[a] Experimental data recommended in ref 30.

3. Theoretical Results

To test our prediction for the yet unknown O_4^{2+} dication, we also performed calculations for S_4^{2+} and Se_4^{2+} dication, which have been well characterized. Optimized geometries and harmonic frequencies for all three of the dications at the B3LYP/6-311+G* and CCSD(T)/6-311+G* levels of theory together with the experimental data are presented in Table 1. To test applicability of these two theoretical methods we performed additional calculations for O_4^{2+} at the RHF/6-311+G* and CASSCF(8,8)/6-311+G* levels of theory and these results are summarized in Table 1. All three dications have the same valence electron configuration: $1a_{1g}^2 1e_u^4 1b_{1g}^2 1b_{2g}^2 1a_{2u}^2 2a_{1g}^2$-$2e_u^4 1e_g^4$. The CASSCF(8,8) calculations for all species used the active space: $2e_u^4 1e_g^4 1b_{2u}^0 3e_u^0 1a_{2g}^0$.

Let us first compare results of our calculation for S_4^{2+} and Se_4^{2+} dications, where solid-state experimental data as well as good ab initio data are available. Optimized S−S and Se−Se bond are in a good agreement at two levels of theory (B3LYP/6-311+G* and CCSD(T)/6-311+G*) and they also agree well with various, previous DFT calculations[30,31] and QCISD calculations.[31] However, the calculated S−S and Se−Se bonds are longer by about 0.06 Å than the corresponding experimental values (Table 1), which can be partially a result of the influence of the environment in the crystals. Calculated harmonic frequencies for S_4^{2+} and Se_4^{2+} are also in good agreement with the average experimental frequencies taking into account that our frequencies are harmonic and also our calculations are done for the isolated species, whereas experimental data are from the solid state. This good agreement provides us hope that molecular properties of the O_4^{2+} dication can also be reasonably evaluated at these levels of theory.

We calculated the geometry and frequencies at the four levels of theory (Table 1). The O−O bond is substantially shorter and frequencies are substantially higher at the RHF/6-311+G* level of theory than at higher levels of theory. The CASSCF(8,8)/6-311+G* calculations yield slightly longer O−O bond and somewhat softer harmonic frequencies. The Hartee−Fock wave function is dominant (C_{HF} = 0.938) in the CASSCF(8,8) expansion. This is similar to the CASSCF(8,8)/6-311+G* calculations for S_4^{2+}, where C_{HF} = 0.947. The most significant contributions beyond the Hartree−Fock configurations come from two configurations corresponding to the excitation of a pair of electrons from the doubly degenerate HOMO ($1e_g$) into the LUMO ($1b_{2u}$). The coefficients for these two configurations were found to be −0.211. At the CCSD(T)/6-311+G* level of theory the O−O bond is now 0.12 Å longer than at RHF/6-311+G* and harmonic frequencies have softened significantly (Table 1). The CCSD(T)/6-311+G* results are in a reasonable agreement with the B3LYP/6-311+G* data. The calculated R(O−O) = 1.383 Å in the O_4^{2+} dication is appreciably shorter than a single bond, R(O−O) = 1.459 Å in hydrogen peroxide HOOH, but it is to a similar degree longer than a double bond, R(O═O) = 1.211 Å in O_2 (all data at CCSD(T)/6-311+G*). The discrepancy between the CASSCF(8,8) calculation and the other correlation methods occurs because of the limited active space, which gives quite a small correlation energy. We were able to optimize the geometry of O_4^{2+} for a larger active space at the CASSCF(10,11)/6-311+G* (number of configurations N = 106,953) level. Here the optimized R(O−O) = 1.329 Å approaches that of the higher levels of theory. The Hartree−Fock configuration is again the dominant configuration in the CASSCF expansion with C_{HF} = 0.917. Further, we optimized the geometry with the more accurate CASSCF(8,8)-MRCISD method. This optimized R(O−O) = 1.342 Å (E_{tot} = −298.668111 au) is in good agreement with the other high-order correlation methods. As before the Hartree−Fock configuration is dominant with C_{HF} = 0.922. Taking into account that the CCSD(T) and B3LYP methods gave us good results for S_4^{2+} and Se_4^{2+}, we believe that our results for O_4^{2+} at the CCSD(T)/6-311+G* and B3LYP/6-311+G* levels of theory could be considered as reasonable estimates. The planar square structure is a local minimum at all employed theoretical levels thus providing us with a hope that inorganic salts of the O_4^{2+} dication might also be made.

We also optimized geometries at the B3LYP/6-311+G* level of theory for a variety of alternative O_4^{2+} structures reported previously for the S_4^{2+} dication.[25,29,30] Results of our calculations are summarized in Figure 1. One can see that the two found alternative local minima are substantially higher in energy than the planar square structure. We were not able to locate any local minima corresponding to the zigzag cis or trans structures at the B3LYP/6-311+G* level of theory for O_4^{2+}.

It was previously shown, that S_4^{2+} and Se_4^{2+} are not thermodynamically stable species toward the dissociation: $S_4^{2+} \rightarrow 2S_2^+$ $\Delta E = -103$ kcal/mol and $Se_4^{2+} \rightarrow 2Se_2^+$ $\Delta E = -78$ kcal/mol.[30] The O_4^{2+} dication is also highly unstable toward dissociation: $O_4^{2+} \rightarrow 2O_2^+$ ($\Delta E = -250$ kcal/mol at the CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G* level of theory). This high exothermicity represents a great challenge for making solid compounds containing O_4^{2+}. One needs to find first a very strong electron acceptor to form a charge-transfer complex with the O_4 group. Also lattice energy should contribute appreciably

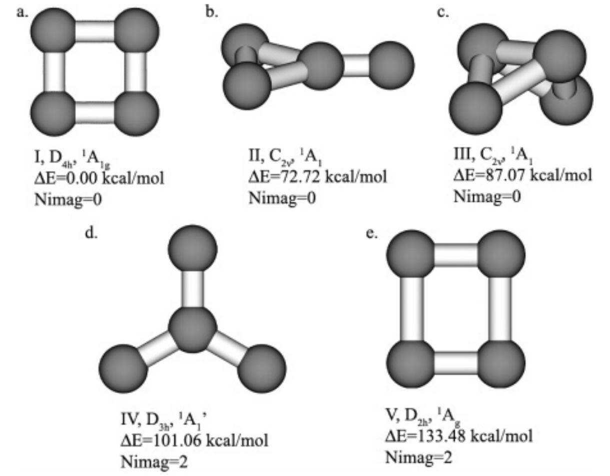

Figure 1. Optimized alternative structures of the O_4^{2+} dication at the B3LYP/6-311+G* level of theory.

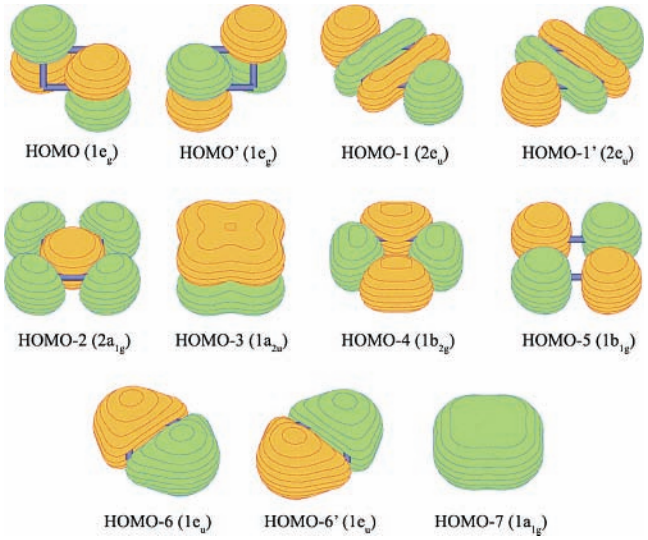

Figure 2. Valence molecular orbitals of the D_{4h} ($^1A_{1g}$) structure of the O_4^{2+} dication.

in order to make a solid material stable. We proposed more than twenty years ago a simple formula for search of strong electron acceptors (superhalogens),[54−57] which may help to identify possible candidates. Another way to probe the planar tetraoxygen dication could be a double-photoionization process of the $(O_2)_2$ dimer. Both approaches are very challenging.

4. Chemical Bonding in the Planar O_4^{2+} Dication

Chemical bonding in the planar M_4^{2+} dications (M = S, Se, and Te) have been previously discussed, and it was pointed out that these species possess 6 π electrons and therefore according to the $4n + 2$ Huckel rule are aromatic.[24] Because the O_4^{2+} dication has the same electronic configuration, one should expect that this dication also is aromatic. Indeed, valence molecular orbitals for O_4^{2+} presented in Figure 2 clearly show the presence of three π-MOs (HOMO and HOMO-3); thus, the dication satisfies the $4n + 2$ rule and it is the first all-oxygen aromatic species. We also probed aromaticity in O_4^{2+}, as well as in S_4^{2+} and Se_4^{2+}, using the NICS proposed by Schleyer and coworkers[51] as a simple computational test for aromaticity. This method calculates the absolute magnetic shielding in centers of rings. A negative value denotes aromaticity. Results of our calculations are summarized in Table 2. Indeed, calculated NICS indices above the O_4^{2+} square clearly shows the aromatic nature of the dication. Surprisingly, the NICS indices for S_4^{2+} show very small negative values, indicating lesser degree of aromaticity than in O_4^{2+} and Se_4^{2+}.

TABLE 2: Calculated NICS Indices for O_4^{2+}, S_4^{2+} and Se_4^{2+}

R,[a] Å	O_4^{2+}, ppm	S_4^{2+}, ppm	Se_4^{2+}, ppm
$B_q = 0.0$	4.3	2.1	−3.3
$B_q = 0.2$	2.7	2.0	−3.3
$B_q = 0.4$	−0.7	1.6	−3.0
$B_q = 0.6$	−3.5	0.9	−2.7
$B_q = 0.8$	−4.6	0.2	−2.5
$B_q = 1.0$	−4.5	−0.5	−2.4
$B_q = 1.2$	−3.9	−1.1	−2.3
$B_q = 1.4$	−3.1	−1.4	−2.3
$B_q = 1.6$	−2.5	−1.5	−2.2
$B_q = 1.8$	−2.0	−1.5	−2.0
$B_q = 2.0$	−1.6	−1.3	−1.8

[a] Distance of the probe above the center of the square.

5. Conclusions

We performed a series of conventional ab initio calculations on the series of the M_4^{2+} dications (M = O, S, and Se) and all our results clearly show the presence of the local minimum planar square structure in agreement with previously reported results for S_4^{2+} and Se_4^{2+}. Calculated geometry and harmonic frequencies for the isolated S_4^{2+} and Se_4^{2+} dications were found to be in a reasonable agreement the corresponding values of these dications in crystal salts, giving us a hope that our calculated O_4^{2+} dication molecular parameters similarly could be a reasonable approximation. The calculated $R(O-O) = 1.383$ Å in the O_4^{2+} diction is appreciably shorter than a single bond, $R(O-O) = 1.459$ Å in hydrogen peroxide HOOH, but longer than a double bond, $R(O{=}O) = 1.211$ Å in O_2 (all data at CCSD(T)/6-311+G*). The square planar structure of the O_4^{2+} dication and its intermediate between single and double O−O bond length can be explain on the basis of aromaticity.

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