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On the Thermodynamic Stability of ArO_4

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The argon tetroxide molecule, ArO_4, and the *isoelectronically* associated perchlorate, ClO_4^-, and sulfate, SO_4^{2-}, ions are investigated on different levels of ab initio theory. The equilibrium structures, harmonic vibrational frequencies, and heats of formation are computed applying density functional theory, second order Møller-Plesset perturbation, singles and doubles coupled-cluster with triples corrections, and Bruekner's doubles coupled-cluster with triples corrections methods in conjunction with various one-particle basis sets. The calculations demonstrate that the description of the bond characteristics in argon tetroxide is sensitive to the applied level of theory. A careful analysis of the global potential energy surface shows that a stationary point exists for the ArO_4 complex corresponding to a local mininium. The calculated equilibrium Ar-O bond distance of 1.48 Å for this structure is slightly longer than the corresponding bond length of the perchlorate ion. Harmonic frequencies for ArO_4 obtained using Bruekner's doubles coupled-cluster with triples corrections are found to have a similar pattern like those obtained for the *isoelectronic* series of ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-. Using the concept of an *isodesmic* reaction, the enthalpy of formation of ArO_4 is determined to be endothermic by as much as 1246 kJ/mol. The present theoretically predicted strong endothermicity and the large Ar−O bond distance are in conflict with the monotonic trends obtained for the *isoelectronic* ions, but can be supported by other chemical extrapolation schemes.

1. Introduction

Ab initio methods have served in the past as valuable tools assisting in the interpretation of experimental results. Especially the interpretation of molecular spectra with the help of ab initio calculations has been of fundamental importance. But in spite of its valuable contributions, theory does seem to take mostly a back-seat position in the sense that the experiment is performed first and that theory and its computational results are used only afterwards to rationalize the previous experimental findings. More recently, however, an increasing number of successful attempts have been made to reverse this process and to use ab initio approaches for predictive purposes. To do this, though, the theoretical chemist must be equipped with some chemical intuition to assure a reasonable success rate between reliable theoretical predictions and the consumed computer time.

Almost all possible pair combinations of atoms from the periodic table have been investigated in the past by ab initio methods. These calculations were generally performed in a brute-force approach and resulted occasionally in predicting some previously unknown stable diatomic compounds. To a much lesser extent this has also been done for triatomic systems. However, as the number of atoms in a molecular ensemble grows, the brute force approach starts to become impossible, and simple empirical schemes are often useful to give directions for detailed theoretical studies. A valuable concept for this purpose is the *isoelectronic* or *isosteric* principle. It has been introduced by Langmuir in 1919[1] in order to rationalize similarities of molecular species consisting of an equal number of electrons and nuclei, and it was frequently used in the past to derive regularities for various groups of chemical compounds and to predict trends for unknown molecular properties. Among others, Pyykkö and co-authors[2,3,4] have successfully applied this scheme, performing calculations at the MP2/6-31G* level of theory, and a number of so far unknown new species were actually predicted in these investigations.

Making use of the *isoelectronic* principle in studying the ArO_4 complex, the attempt can be made to predict its structural parameters and thermodynamic stability by extrapolation from the *isoelectronic* series of ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-. Essentially symmetrical tetrahedral geometrical structures are found for these anions with the four oxygens at the edges of the regular tetraeder and the third-period atoms (Si, P, S, Cl) at its center. The bond lengths between the central atoms and the oxygens are monotonically decreasing in the series because of the decreasing size of the central atoms with increasing nuclear charges and as a result of the continuous change of the bond character from SiO_4^{4-} with a predominant single-bond structure to the other ions with increasing double-bond contributions. Fitting the experimentally determined bond lengths of the ions (silicate, 1.63 Å; phosphate, 1.55 Å; sulfate, 1.50 Å; perchlorate, 1.46 Å) vs. the charge by simple linear or exponential functions, the bond length in ArO_4 can be extrapolated to be approximately 1.41 Å. Similar extrapolations can in principle be done to predict the thermodynamic stability of the rare, gas compound using experimental enthalpies of formation for the *isoelectronic* anions. However, since these enthalpies of formation cannot be measured directly, the numbers available from the literature

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depend on the theoretical model and different assumptions used to derive these quantities from other experimental information, and they often vary over fairly large ranges. From the enthalpies of the ionic series the ΔH_f for ArO_4 can thus be only estimated to be approximately thermoneutral. Actually the multiply charged species, especially the higher ones, are not stable in isolated form in the gas phase, and their thermodynamic stability can thus only be determined, indirectly from measurements in crystalized or solvated environments. Because of these basic difficulties, a reference system of neutral compounds would be preferable for which the ΔH's can be measured directly. A suitable *isoelectronic* series in this context is the sequence of neutral stable gases SiF_4, POF_3, SO_2F_2, ClO_3F. In this series, starting from SiF_4, the fluorine atoms are replaced in a stepwise fashion by oxygens, leading finally to the ArO_4 complex. Apart from the regular tetrahedral geometry of the silicon compound the other members have distorted structures with X−O bond distances of d(P−O) = 1.436 Å, d(S−O) = 1.405 Å, and d(Cl−O) = 1.404 Å. The thermodynamic stability of the compounds decreases rapidly from the highly stable SiF_4 (−1615 kJ/mol), and POF_3 (−1254 kJ/mol) to SO_2F_2 (−760 kJ/mol) and ClO_3F (approximately −390 kJ/mol, derived from bond strength data since the directly measured low $\Delta H_f(ClO_3F) = -24$ kJ/mol seems to be questionable) and can be extrapolated to an approximately thermoneutral value for ArO_4. The fact that in both extrapolations the formation of the ArO_4 complex is predicted to be thermoneutral or eventually endothermic reflects the general expectation that the Ar-O bond is much weaker than the corresponding X−O bonds (X = Si, P, S, Cl) in each of the above *isoelectronic* series.

It is worth noticing at this point that the experimentally well-known XeO_4 was found to be stable but endothermic by about +643 kJ/mol. The corresponding intermediate fourth-period rare gas compound, KrO_4, on the other hand, is generally assumed to be less stable according to the chemical experience that the fourth-period elements have much higher oxidation potentials compared with those in the third and fifth periods ("d-shell contraction" effect).

In the present study different ab initio methods are applied to calculate the optimized structure and the thermodynamic stability of ArO_4. In order to assess the reliability of the theoretical results, identical calculations are performed for the ClO_4^- and SO_4^{2-} ions for which the theoretical values can be compared with available experimental data. The results of the present calculations are used to discuss limitations of the *isoelectronic* principle when making quantitative predictions from extrapolations.

2. Methods and Computational Details

Various ab initio techniques are employed in the present study. Initial investigations of the equilibrium structures and enthalpies of formation are performed at the Møller−Plesset MP2 and the density functional DFT (B3LYP[5,6,7] and BP86[8,9]) levels of theory using standard basis sets of the 6-31G* type. To assess the need of diffuse functions in the one-particle basis sets, some calculations also used a 6-31+G* basis set. In the MP2 and DFT calculations, the default options provided in the Gaussian program package are used. In addition, calculations at the CCSD(T) level of coupled-cluster theory, and with its BCCD(T) Brueckner version,[10−15] are done employing large ANO basis sets[16,17] to improve the low-level results for the equilibrium structures and enthalpies of formation. Especially the BCCD(T) version was previously found to be able to handle systems with symmetry breaking problems (see for example the study on symmetry breaking problems in O_4^+[18]) and is therefore used here for geometry optimizations on the higher theory level and to evaluate force constants and harmonic frequencies. The large ANO basis sets are contracted as Ar,Cl,S(5s4p3d2f) and O(4s3p2dlf) which leads to a total number of 357 functions for the ArO_4 complex and its *isoelectronic* analogues. In the large-scale calculations, the 1s electrons on oxygen and the ls, 2s, and 2p electrons of the third-row elements are frozen in the correlation treatment. The studies are performed using the MOLPRO 96.2[19] or MOLCAS 4.1[20] as well as the Gaussian 94[21] quantum chemistry program packages installed on an IBM RS6000 workstation.

The direct evaluation of the enthalpy of formation for argon tetroxide and for the *isoelectronic* anions according to

$$2O_2 + X^{(n-)} \rightarrow XO_4^{(n-)}\ (X^{(n-)} \equiv Si^{4-}; P^{3-}; S^{2-}; Cl^-; Ar) \tag{1}$$

involves comparisons of the absolute energies of species with entirely different electronic structures and bond properties which causes problems in ab initio calculations aiming at high accuracies. The theoretical description especially of the correlation energy contributions in the triplet open-shell electronic structure of the ground-state oxygen molecule, O_2 ($\tilde{X}\,{}^3\Sigma_g^-$), and the closed-shell electron system of the tetroxide complexes at equal accuracy levels appears to be impossible even when highly sophisticated methods are applied. It is therefore suspected that ab initio determinations of reaction energies in reaction (1) may give unrealistic results.

At this point, the concept of an *isodesmic* reaction comes into play. According to ref 22 this reaction is "an example of chemical changes in which there is retention of the number of bonds of a given formal type, but with a change in their relation to one another". It has previously been shown that ab initio calculated reaction energies for these kinds of reactions can be highly accurate, especially in cases in which the changes in the bond strengths and, therefore, the absolute values of the reaction energies are small.[22] In the present application, the concept is used at the limit of its original definition such that it is simply considered as a reaction in which the number of bonds of a specific type is preserved. Making use of the experimentally known ΔH_f values for ClO_4^- and Cl^-, an *isodesmic* reaction for calculating the heat of formation of ArO_4 can be formulated as

$$ArO_4 + Cl^- \rightarrow Ar + ClO_4^- \tag{2}$$

and a corresponding reaction for the *isoelectronic* anions for instance, is,

$$ClO_4^- + S^{2-} \rightarrow Cl^- + SO_4^{2-} \tag{3}$$

The complication due to the oxygen molecule in the direct evaluation according to eq 1 is completely eliminated in this scheme, and comparisons are now made between systems with similar electronic and bond structures.

For the series of anions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^- the experimental fundamental vibrational frequencies are only slightly changing. This may be used as an indication that for these species the reactions corresponding to eq 3 can be assumed to be *isodesmic*, and it is one of the main issues of the present study to check if this also holds for the reaction in eq 2 involving the ArO_4 complex. The effects due to differences between the zero-point vibrational energies of the different molecular species in the reaction equations are usually small compared with the inaccuracies connected with reaction-energy determinations.

TABLE 1: Comparison of Experimental and Theoretical Equilibrium Bond Lengths (in Ångströms) Obtained at Different Levels of Ab Initio Theory

molecule	bond length	comment	reference
SO_4^{2-}:			
	1.495	SCF/TZP	23
	1.521	MP2/6-31G*	
	1.525	B3LYP/6-31G*	
	1.504	BCCD(T)/ANO	
	1.50	expt. average from different sulfates	24
ClO_4^-:			
	1.464	SCF/TZP	23
	1.473	SCF/ECP	31
	1.483	MP2/6-31G*	
	1.499	B3LYP/6-31G*	
	1.512	BP86/6-31G*	
	1.461	BCCD(T)/ANO	
	1.464	expt. bond average in NH_4ClO_4	25
ArO_4:			
	1.450	SCF/cc-pVTZ	
	1.48	MP2/6-31G*	26
	1.476	MP2/6-31G*	
	1.549	B3LYP/6-31G*	
	1.566	BP86/6-31G*	
	1.476	BCCD(T)/ANO	

They are therefore neglected here. The largest effect of this kind is expected for reactions according to eq 1 in which the zero-point energy contributions are estimated to increase the enthalpies of formation for ArO_4 and ClO_4^- by approximately 30−50 kJ/mol. Neglecting this effect does not change the conclusion made in this study.

3. Results and Discussion

3.1. Equilibrium Structures. Computed and experimental bond lengths of the sulfate SO_4^{2-} and perchlorate ClO_4^- ions in the gas phase as well as present theoretical results for argon tetroxide, ArO_4, are collected in Table 1. For the sulfate ion, a simple ab initio study at the SCF/TZP level[23] gives an equilibrium S−O bond length of 1.496 Å, in good agreement with the experimental value of 1.50 Å which was derived as an average distance from a number of sulfates.[24] Present calculations at low levels of theory using the MP2/6-31G* and B3LYP/6-31G* schemes both give bond distances that are substantially too long, whereas geometry optimization at the correlated level of theory with the coupled-cluster BCCD(T) method and employing large ANO basis sets leads to a S−O bond length of 1.504 Å, in close agreement with the experimental number. The same trend also holds for the perchlorate ion where the simple SCF/TZP result[23] matches the experimental value of 1.464 Å which is obtained as an average in NH_4ClO.[25] The MP2/6-31G* and the DFT approaches, B3LYP/6-31G* and BP86/6-31G*, fail again seriously producing bond lengths which are much too long, and the BCCD(T) optimization gives a Cl−O bond length of 1.461 Å, perfectly close to the experimental number. For the two ion complexes the present calculations thus show that the DFT schemes have difficulties in describing the bond situation in the tetrahedral ion complexes correctly and that even at the MP2/6-31G* level the optimized distances are noticeably too large by about 0.02 Å.

In a previous theoretical study of ArO_4,[26] it was found that calculations on the Hartree-Fock level using a 6-31G* basis set did not lead to a stable structure, whereas a geometry optimization on the MP2 level gave an equilibrium distance of 1.48 Å. These results are verified in the present study, but it is also shown here that a SCF calculation using a larger basis set, cc-pVTZ,[27,28] which is equivalent to the SCF/TZP of ref 23 does give a stable structure with a bond length of 1.45 Å. This indicates that the 6-31G* basis set is insufficient on the SCF level to stabilize the ArO_4 complex, but that this basis set deficiency is fortuitously compensated when correlation effects at the MP2 level are included. Additional calculations performed here with the two DFT approaches both give bond lengths that exceed the MP2 results by more than 0.07 Å. Geometry optimization at the correlated level of theory employing large ANO basis sets, BCCD(T)/ANO, gives finally an Ar−O bond length of 1.476 Å. This value is the most reliable theoretical prediction of the bond distance in ArO_4 and the fact that MP2/6-31G* gives an identical result has to be considered as a coincidence.

The theoretically predicted Ar−O bond length is thus slightly longer than the corresponding distance in ClO_4^-, and it is obviously much longer (∼0.07 Å) than the value extrapolated from the experimental bond distances of the *isoelectronic* series of anions. Assuming that the theoretical result is correct it turns out that within this *isoelectronic* series the bond length values first decrease monotonically before they pass through a minimum for the ClO_4^- ion and rise again for ArO_4. Similar trends were actually observed in previous studies of various other *isoelectronic* systems.[2,3,4] It is also interesting to note here that the same deviation from a purely monotonic trend has been observed before for *ortho*-xenates, XeO_6^{4-}. The experimental bond length of 1.84 Å obtained for this complex is slightly longer than the 1.82 Å found for *ortho*-periodates, IO_6^{5-} whereas an isoelectronic extrapolation would lead to a shorter distance.

3.2. Harmonic Frequencies. The evaluation of the harmonic frequencies is often used as a critical test when studying the stability of unknown species. Technically these calculations are performed by applying a gradient optimization procedure which searches for a stationary point on the global potential energy surface and evaluates at this point the vibrational frequencies within the harmonic approximation. The fact that in the case of ArO_4 real values for the frequencies are obtained for all vibrational modes indicates that the associated optimized structure of the complex corresponds to a local minimum on the potential surface. Whereas initial optimizations on the CASSCF level of theory were affected by symmetry breaking problems and failed to provide a stable T_d structure for ArO_4 (small deviations up to about 0.2 degrees in the bond angles are obtained), the coupled-cluster approaches succeeded in predicting a stable structure in the correct point group and especially the BCCD(T) version was employed for the numerical evaluation of the force constants.[18]

The computed frequencies of the perchlorate ion and the argon tetroxide complex are collected in Table 2 together with previous theoretical and experimental data for the *isoelectronic* ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-. The results of the earlier studies show that the vibrations of the different molecules in this series are rather well-behaved and that already the low SCF level theory can provide fairly good agreement with experiment. Very good agreement is observed when comparing the experimental results of Eysel[29] with the present BCCD(T) results for the perchlorate ion. It is therefore expected that a similar quality of agreement between theory at the BCCD(T) level and the genuine vibrational frequencies also holds for the ArO_4 molecule.

Inspection of the results in Table 2 also shows, however, that for argon tetroxide the order of the two lowest frequencies is

TABLE 2: Experimental and Theoretical Vibrational Frequencies (in cm^{-1}) for the Silicate, Phosphate, Sulfate, and Perchlorate Ions and for Argon Tetroxide

molecule	E	T_2	A	T_2	comment
SiO_4^{4-}:	500	625	800	1050	fundamentals[30]
PO_4^{3-}:	358	500	970	1080	fundamentals[30]
SO_4^{2-}:	450	611	983	1105	fundamentals[30]
	468	668	1025	1214	harmonic, SCF/6-31G*[23]
ClO_4^-:	459	625	928	1119	fundamentals[30]
	464	631	937	1124	fundamentals[29]
	459	635	928	1126	fundamental, SCF/ECP[31]
	478	668	975	1188	harmonic, SCF/6-31G*[23]
	463	588	863	1122	harmonic, BCCD(T)
ArO_4:	477	377	725	918	harmonic, BCCD(T)

interchanged compared with the sequence found for the *isoelectronic* ions. In ArO_4 the lowest frequency is in the T_2 irreducible representation whereas all the other members of the series have a lowest E type mode. This sequence change may be of some significance and could indicate that the lowest accessible decomposition channel for the argon compound is different from those for the ionic species.

The experimental fundamental frequencies of the ion complexes are fairly similar for each type of vibrational mode,[30] which indicates that the bond strengths and their characteristics do not change much within the *isoelectronic* series. It was already mentioned above that this can be used as an indication that the reactions between pairs of the ions according to eq 3 may be assumed to match the conditions for an *isodesmic* reaction. The closest agreement of frequencies actually exists between the sulfate and the perchlorate ions. In the case of the ArO_4 the present calculations at the BCCD(T) level determine harmonic frequencies which are lower by about 150−200 cm^{-1} relative to the corresponding ClO_4^- frequencies except for the E type mode (which causes the sequence change). These frequency lowerings have to be interpreted such that they reflect the weakening of the bonds in the ArO_4 complex due to the rare gas character of the central Ar atom. Even if they are not very large this could have the consequence that because of the different bond strengths in ClO_4^- and ArO_4 the conditions for the *isodesmic* character of reaction (2) are not quite fulfilled and that the reliability of the ΔH_f prediction for ArO_4 is thus reduced.

3.3. Enthalpies of Formation. Conventionally the enthalpies of formation of chemical compounds are calculated according to their direct formation reactions. As a test for the reliability of this approach, the enthalpy of formation of the perchlorate ion ClO_4^- is calculated here according to eq 1 and compared with values derived from experiments.[23,29,31] For this purpose the energies of the relevant species are evaluated at different levels of ab initio theory, and the resulting reaction heats are used to determine the enthalpy of formation for ClO_4^- employing the experimental ΔH_f value for Cl^-. All energy values obtained from the present ab initio calculations are listed in Table 3, and the experimental ΔH_f data[32−37] used in this study are collected in Table 4. According to the calculated $\Delta H_f(ClO_4^-)$ values for the direct formation reaction (eq 1) the formation of ClO_4^- would be close to thermoneutral at the MP2/6-31G*, B3LYP/6-31G*, and BP86/6-31G* levels of theory, which disagrees with experimental evidence. The discrepancy cannot be explained by a deficiency of the one-particle basis in the sense that it does not contain a sufficient number of diffuse functions. Actually augmenting the basis set by additional diffuse functions, a calculation at the MP2 level (MP2/6-31+G*) increases the enthalpy of formation of the ClO_4^- ion from −20 to +6 kJ/mol. Keeping in mind that a (6-31G*) basis set is far from being complete, this effect is easy to explain such that the straightforward addition of further diffuse functions leads to an energy lowering especially of the Cl^- ion. However, it was already stated above that the failure of the direct determination has to be attributed to the unbalanced treatment of the electron correlation in the open-shell oxygen molecule relative to the other closed-shell species in eq 1. Actually, the electron correlation contributions in the two O_2 ($^3\Sigma_g^-$) molecules are overestimated relative to the closed-shell systems which leads to the endotermic (negative) reaction energies for the ClO_4^- formation listed in Table 3, whereas application of the experimental ΔH_f values for Cl^- and ClO_4^- would give an exothermic ΔE of +116 kJ/mol. This shows that the earlier attempt[26] to investigate the stability of the ArO_4 complex by the direct approach according to the formation reaction (eq 1) is unrealiable.

In the present study the attempt is made, instead, to investigate the thermodynamic stability of ArO_4 making use of the *isodesmic* reaction (2). The relevant energies in Table 3 and the experimental enthalpies in Table 4 are taken to determine the reaction heat and enthalpy of formation for ArO_4. The results obtained at the different levels of theory applied in this study are located to Table 3. The ΔE at all levels have large positive values which means that the reverse reaction, the formation of ArO_4 from ClO_4^-, is strongly endothermic. At the most reliable theory levels, coupled-cluster calculations determine the enthalpy of formation of ArO_4 to be +1246 kJ/mol (BBCD(T)) and 1222 kJ/mol (CCSD(T)) which is substantially lower than the previously published value of 17.3 eV (≡ 1664 kJ/mol).[26] The endothermic character of ArO_4 relative to ClO_4^- has to be assigned to the rare gas character of the argon atom and its large ionization potential of 15.8 eV.[32] In the present usage of the *isodesmic* concept it is true that in reaction (2) the number of tetrahedral bonds is unchanged, but the central bonding atoms are different and, in contrast to the rare gas atom, the electronic system in the Cl^- ion is more easily polarizable by the surrounding oxygens. Because of the large reaction energy of reaction (2), the reliability of the enthalpy determination of the rare-gas complex is possibly reduced. In the above discussion of the harmonic frequencies, the lowering of the ArO_4 frequencies relative to the ClO_4^- results was interpreted to be due to a weakening of the Ar−O bonds. The difference in the bond energies of the tetrahedral Cl−O and Ar−O bonds is obtained here at the BCCD(T) level to be 340 kJ/mol. The average bond strengths in ClO_4^- and ArO_4 are determined as 278 and −63 kJ/mol, respectively, whereas, for comparison, the bond strength in the oxygen molecule is 498 kJ/mol. Apart from the large endothermicity of ArO_4 relative to ClO_4^- the unfavorable bond strength value also indicates that the rare-gas complex could possibly have a short lifetime.

To check the reliability of the present attempt to predict ΔH_f for ArO_4 theoretically, it is useful to compare the theoretical ΔH results for a closely related reaction with the corresponding values derived from experiment. A perfectly suitable reaction for this purpose is the *isodesmic* conversion of perchlorate to sulfate ions described in eq 3. Various $\Delta H_f(ClO_4^-)$ and $\Delta H_f(SO_4^{2-})$ values are found in the literature and are listed in Table 4. The corresponding information, however, for the S^{2-} ion is not available. This ion does not exist in isolated form in the gas phase but it is stable in crystalized environments such as in a CaS crystal. The $\Delta H_f(S^{2-})$ can therefore be derived from experimental data applying the Born-Haber ionic model which has been developed for calculating cohesive energies in solids.

TABLE 3: Ab initio Total Energies (in Hartree units) of Ground State Atomic and Molecular Species in Reactions (1), (2), (3) (see text) and Related Atomic Species Together with Derived Heats of Reaction (Δ*E* in kJ/mol) and Enthalpies of Formation (ΔH_f in kJ/mol)

species	MP2[a]	B3LYP[a]	BP86[a]	BCCD(T)[b]	CCSD(T)[b]
SO_4^{2-}:				−698.231 955	−698.260 883[c]
ClO_4^-:	−759.472 267	−760.798 441	−760.871 662	−760.067 051	−760.104 722[c]
ArO_4:	−826.152 386	−827.546 545	−827.651 869	−826.796 575	−826.848 807[c]
S^{2-} (^1S_g):				−397.563 846	−397.743 660
S^- (^2P_u):					−397.889 633
S (^3P_g):					−397.817 936
Cl^- (^1S_g):	−459.652 104	−460.252 233	−460.279 285	−459.808 774	−459.973 449
Cl (^2P_u):					−459.844 448
Ar (^1S_g):	−526.911 053	−527.547 540	−527.517 145	−527.056 521	−527.225 528
Ar^+ (^2P_u):					−526.651 498
O_2 ($^3\Sigma_g^-$)[d]:	−149.949 732	−150.320 038	−150.330 337		
eq 1					
Δ*E*	−208	−246	−179		
$\Delta H_f(ClO_4^-)$	−20	18	−49		
eq 2					
Δ*E*	1520	1437	1202	1361	1334
$\Delta H_f(ArO_4)$	1405	1322	1087	1246	1222
eq 3					
Δ*E*				1076	1013
$\Delta H_f(S^{2-})$				480	418

[a] Using the 6-31G* basis sets. [b] Using the extended ANO basis sets. [c] Calculated at the BCCD(T) optimized geometies and with only the (1s) orbitals uncorrelated. [d] Calculated at the unrestricted levels: UMP2, UB3LYP, and UBP86, respectively.

TABLE 4: Enthalpies of Formation (in kJ/mol): Literature Values and Estimated Values Derived from Other Experimental Data

molecule	ΔH_f	reference
SO_4^{2-}:	−711.	33
	−758.	34
ClO_4^-:	−343.08	32
	−344.	35
	−235.6 ± 0.8	36
	−384.9 ± 20.9	37
S^{2-}:	≤700	estimated (see text)
Cl^-:	−228.028	32
Ar:	0.0	by definition
O_2:	0.0	by definition

The enthalpy of formation of CaS, for example, can be decomposed according to the following expression

$$\Delta H_f(\mathrm{CaS}) = \Delta H_f(\mathrm{Ca}^{2+}) + \Delta H_f(\mathrm{S}^{2-}) + E_{BH} + E_{vdW} \quad (4)$$

in which the enthalpies of the ions consist of the corresponding atomization energies plus the ionization energy or electron affinity, respectively. The van der Waals energy, E_{vdW}, contains the weak attractive induction forces and is usually approximated making use of the evaporation energies of the corresponding isoelectronic rare-gas atoms, i.e., in the CaS case, of two argon atoms. This small attractive force amounts, then, in the present application to $E_{vdW} = -35.5$ kJ/mol. The Born-Haber energy E_{BH} represents Coulomb attraction and lattice repulsion energies in the solid and can be expressed (in SI units) as

$$E_{BH} = \frac{1}{4\pi\epsilon_0} N_L\, M_k \frac{Z^2 e^2}{d_0}\left(1 - \frac{1}{n}\right) \quad (5)$$

Here ϵ_0 is the electric field constant and in the present unit system the first term becomes $(1/4\pi\epsilon_0) \approx 9 \times 10^9$. N_L is the Loschmidt number, and M_k the Madelung constant. This constant depends only on the geometry of the crystal lattice, and since CaS crystallides indentically to NaCl, the $M_k(\mathrm{NaCl}) = 1.748$ is used here. In the Coulomb term, the parameter d_0 in the denominator represents the average distance in the crystal between an ion and its nearest neighbors with opposite charges ($d_0 = 2.847$ Å in CaS) and *Z* the effective charge on the ionic centers in the solid. The (1/*n*) term introduces lattice repulsion effects with *n* being the repulsion constant. Values for *n* are usually in the range between 8 and 12, and here the NaCl value of $n = 9.3$ is employed. Using the above values for the various parameters in eq 5, the Born-Haber energy for CaS amounts to $E_{BH} = -3045$ kJ/mol assuming full ionization ($Z = 2$) in the crystal. With this number and with the experimental enthalpies $\Delta H_f(\mathrm{CaS}) = -473$ kJ/mol and $\Delta H_f(\mathrm{Ca}^{2+}) = +1913$ kJ/mol the formation enthalpy for S^{2-} is obtained with a strongly endothermic value of +695 kJ/mol. Since the total value of all the constant factors in eq 5 is rather large ($\approx 1.39 \times 10^3$), already small variations of the remaining parameters, M_k, d_0, *n*, and especially of *Z*, have strong effects on E_{BH}. Assuming, for instance, that the ionization level in the CaS crystal would be only slightly changed to about 95 percent ($Z = 1.90$), this will reduce the endothermic $\Delta H_f(S^{2-})$ value by almost exactly 300 kJ/mol. Since many formation enthalpies of ionic species are derived making use of the Born-Haber model, their magnitudes are heavily dependent on the actual choice of the parameter values in eq 5. This essentially explains that so-called experimental ΔH_f data found in the literature are often scattered over a fairly large range.

Because of this difficulty in obtaining a reliable estimate of the formation enthalpy $\Delta H_f(S^{2-})$ from the above equations, a different scheme to derive this quantity is also considered here. According to this model, the formation of the S^{2-} ion from solid sulfur can be divided into three steps: (i) Atomization of $S_8/S_6 \rightarrow S$ requires an atomization energy of +279 kJ/mol. (ii) Attachment of the first electron to the sulfur atom is exothermic by an energy amount equal to the first electron affinity of S, EA(S) = −200 kJ/mol. (iii) Addition of the second electron gives rise to two energy effects, the shell completion energy of −349 kJ/mol (assumed to be equal to EA(Cl)) and the Coulomb repulsion energy of +817 kJ/mol (calculated for an assumed radius of S^{2-} of 1.7 Å which is taken from the CaS crystal). Summation of these energy contributions leads to a formation enthalpy of $\Delta H_f(S^{2-}) = +547$ kJ/mol. Using this value in eqs 4 and 5, an ionization level in CaS of 97 percent is obtained, which is a very reasonable result. From the two energy contribution in the third step of the above scheme, a value for the second electron affinity can be derived as EA2(S) = +468 kJ/mol. This value is, of course, hypothetical because it only holds under the assumption that the two electrons are artificially kept within a sphere around the nuclear center with a radius of 1.7 Å. Free S^{2-} ions in the gas phase however are unstable because of the Colomb repulsion between the second electron and the singly charged S^- ion, and the interaction energy (i.e., the second electron affinity) is vanishing $\lim_{r\to\infty}$ EA2(S) = 0.[38,39]

Turning back now to the *isodemic* reaction,[3] the present calculations at the BCCD(T) level give a reaction energy of 1076 kJ/mol which leads to a $\Delta H_f(S^{2-})$ in the range of 420–500 kJ/mol depending on which ΔH_f values for the other reaction partners are used. The agreement with the above empirically derived formation enthalpy for the S^{2-} ion is reasonable in spite of the fairly large reaction energy for this reaction. This means that also for reaction (2) for which the reaction heat is 1360 kJ/mol, the predicted ΔH_f (ArO_4) value should also be fairly reliable, with an estimated uncertainty range of about ±300 kJ/mol. Additional checks of the quality of the present ab initio calculations were performed calculating at the CCSD(T) level with the large ANO basis the ionization potential of Ar as well as the electron affinities for Cl and S. The theoretical results are in good agreement with the experimental numbers (in parentheses): IP(Ar) = 15.62 eV (15.755 eV), EA(Cl) = 3.51 eV (3.61 eV), EA(S) = 1.95 eV (2.07 eV). From the difference of the ab initio calculated energies of the S^- and S^{2-} ions a value of +390 kJ/mol can be obtained for the second electron affinity of sulfur. This is rather close to the above empirical result. A graphical representation of the corresponding ANO basis set wave function or the related electron density shows that it does not spread out too far from the nuclear center. Extension of the basis set by adding more diffuse functions increases the function space and causes the second electron to move further out as a result of the Coulomb repulsion. In the ultimate limit of an infinitely large diffuse basis set, the second electron will thus be completely separated and the energy difference will become zero, $\Delta E(S^- - S^{2-}) = 0$.

4. Summary

Structural and thermodynamic properties of the argon tetroxide complex are calculated in this study in comparison to the isoelectronic perchlorate and sulfate ions which are used as reference systems with well-established experimental and theoretical results for many of their properties. The calculations are done on different levels of ab initio theory in order to be able to estimate the reliability of the theoretical results. Apart from the MP2 method, which is frequently used in similar stability studies of chemical compounds, and apart from fashionable DFT approaches, coupled-cluster schemes such as the CCSD(T) and especially the Brueckner version BCCD(T) are applied here to calculate the equilibrium geometrical structures and the associated energies as well as harmonic vibrational frequencies. The bond length in ArO_4 is optimized at the BCCD(T) level to 1.476 Å, slightly longer than the bond in ClO_4^-, whereas the DFT approaches overestimate the Ar–O bond length by more than 0.07 Å. Gradient calculations show that the optimized equilibrium structure of ArO_4 corresponds to a local minimum on the potential energy surface. The harmonic frequencies obtained for this structure have many characteristics in common with those of the *isoelectronic* series of anions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-. The fact that the sequence of the lowest vibrational modes is changed in ArO_4 could possibly indicate that the rare-gas complex fragments differently from the dissociation processes found for the ionic compounds. It is shown here for the case of the ClO_4^- ion that the evaluation of the enthalpy of formation according to the direct formation reaction[1] employing simple methods like MP2(UMP2) or the DFT approaches leads to significant errors because of the difficulty in treating the electron correlation effects of the molecular systems with totally different bond structures at equal accuracy levels. Applying, instead, the concept of an *isodesmic* reaction for the determination of the thermodynamic stability of the ArO_4 complex, a strongly endothermic enthalpy of formation of approximately 13 eV is derived at the BCCD(T) level. From the ab initio calculated energies for all the reaction partners of this reaction, a rather large reaction energy is obtained. Since, due to this big energy difference and the associated bond strength change, it cannot be excluded that the reliability of the enthalpy prediction for ArO_4 is reduced, test calculations for the closely related reaction[3] are performed. These calculations demonstrate, however, that in this case the enthalpies obtained at both correlated coupled-cluster levels are within the uncertainty range of the experimentally defined values. Additional accuracy checks of the present theoretical treatments are made, calculating on the CCSD(T) level the ionization potential of Ar and the electron affinities of Cl and S. The theoretical results are within about 0.1 eV of the corresponding experimental literature values. This shows the reliability of the calculations on which the results of the present study are based.

It has been stated before[26] that the virtue of theory is to systematize and to predict, and that one of the most simple approaches used by chemists for this purpose is the *isoelectronic* principle. In agreement with a previous series of studies,[2–4] the present calculations support the common experience that the *isoelectronic* principle is a valuable tool for providing qualitative trends for unknown species and their properties, but that care has to be used when trying to make quantitative predictions. Whereas quantitative predictions made by interpolations are usually rather accurate, their reliability becomes less safe if they are obtained by extrapolations, because these are often based on the assumptions that the quantities change in a purely monotonic fashion and that for accurate predictions the data from which the extrapolations are made are available with sufficient accuracy. Both requirements are not always fulfilled as shown in the present study of the ArO_4 complex: (i) linear or exponential extrapolations are schemes that are too simple which do not necessarily represent all cases (actually, in agreement with previous studies, the present bond-length determination for ArO_4 demonstrates that deviations from a pure monotonic rule are quite common); and (ii) while structural parameters are usually available with a fairly good accuracy, thermodynamic quantities like enthalpies of formation are often known only with a rather large uncertainty margin. Therefore, making quantitative extrapolations on the basis of the *isoelectronic* principle can only mean that numerical irregularities are assumed to be improbable. In this sense the bond distance of ArO_4 is predicted from the known lengths of the *isoelectronic* ions to be within about ±0.05 Å of the bond distance in ClO_4^- in full agreement with the result of the present theoretical bond-length optimization. Similarly, the $\Delta H_f(ArO_4)$ would be predicted to be within about ±500 kJ/mol of the ClO_4^- value or within about ±400 kJ/mol of the value for ClO_3F which means essentially that the ArO_4 formation enthalpy can be estimated qualitatively to be about thermoneutral. The calculated strongly endothermic $\Delta H(ArO_4)$ value does not confirm this estimate. Especially with respect to the series of ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-, the present theoretical enthalpy and bond-distance results for the ArO_4 complex do not follow their monotonic trends. Actually, the fact that the Ar−O distance is calculated to be slightly longer than the Cl−O bond length, i.e., much longer (∼0.07 Å) than the value obtained by *isoelectronic* extrapolation, indicates already that the ArO_4 is much less stable than the perchlorate ion. Considering, however, the *isoelectronic* series of neutral gases SiF_4, POF_3, SO_2F_2, ClO_3F, it should be pointed out here that the correct enthalpy value of the chlorine compound is of critical importance in this context. If the low experimental result of $\Delta H_f = -24$ kJ/mol would be accepted, *isoelectronic* extrapolation from this series actually leads to a value for ArO_4 in the range of the present theoretical result. But since this low enthalpy value seems to be in conflict with the experimentally well-known high thermal stability of the ClO_3F gas, additional reliable information for this quantity is still needed before a definite answer can be given.

There are other chemical analogues which can be considered to support the present theoretical finding. In the fifth period, from the series of ions *isoelectronic* with XeO_4, only IO_4^- is stable. For this ion an enthalpy value of ~ -473 kJ/mol can be derived from the experimental $\Delta H_f(KIO_4) = -460$ kJ/mol (with appropriate assumptions for the parameters M_k, d_0, n, and with $Z = 1$ in eq 5). The increase in endothermicity from IO_4^- to XeO_4 is thus rather large, not too different from the one found here for ArO_4 relative to ClO_4^-. Further, in the *isoelectronic* series WO_4^{2-} ($\Delta H_f = -1620$ kJ/mol), ReO_4^-, ($\Delta H_f = -1113$ kJ/mol), and OsO_4 ($\Delta H_f = -390$ kJ/mol), a large endothermicity increase is observed when moving from the negative ions to the neutral OsO_4 compound. This resembles once more the much more drastic situation encountered here for ArO_4 in comparison with the enthalpies of the *isoelectronic* series of anions. Comparing, finally, the enthalpies in the *isodesmic* reactions (2) and (3), trends are observed which also support the theoretical prediction derived for ArO_4. In reaction (3) the transition from the highly unstable S^{2-} to the very stable SO_4^{2-} complex is accompanied by a large exothermic change of the corresponding enthalpies of more than −1000 kJ/mol. The corresponding change from Cl^- to ClO_4^- is much less exothermic. Using the numbers in Table 4, this difference amounts only to slighly more than −100 kJ/mol. When extrapolating to the Ar case, it turns out that the large endothermic enthalpy result calculated for ArO_4 follows exactly this trend. And it is interesting to note that a similar trend exists for the corresponding fifth-period compounds. Differences between the formation enthalpies (given in parenthesis) for the systems Te^{2-}/TeO_4^{2-} (~ -800 kJ/mol), I^-/IO_4^- (∼285 kJ/mol); and Xe/XeO_4 (+643 kJ/mol) show a similar but less pronounced behavior as described above for the third period.

One of the reviewers of this paper has raised the question whether the comparison made in this study between the anions ClO_4^-, or in particular SO_4^{2-} and the neutral ArO_4 is appropriate since the anions are characterized by very diffuse charge densities in contrast to the different situation in ArO_4. The results of the present calculations show, indeed, that the characteristics of the rare-gas compound cannot be easily extrapolated from those of the *isoelectronic* ions. Its bond lengths do not follow the monotonic trend of the ionic analogues, and for its formation enthalpy, a large endothermic jump is obtained. A number of corresponding cases with similar deviations from simple monotonic trends are given in the above discussion. On the other hand, a comparative analysis of the canonical orbital bases generated for the coupled-cluster calculations of ArO_4 and the *isoelectronic* ions shows that there is no drastic change in the bonding mechanisms. In the simplified picture of the Mulliken atomic population analysis, the extra negative charge of the ions is located on the oxygen centers, and in addition, the bonds are polarized such that there is a charge deficiency on the central atom: $\Delta(S) = +1.6$ and $\Delta(O) = -0.9$ for SO_4^{2-} and $\Delta(Cl) = +1.8$ and $\Delta(O) = -0.7$ for ClO_4^-. The situation in the neutral ArO_4 is similar, except that the surplus of negative charge on the oxygens is now smaller: $\Delta(Ar) = +1.7$ and $\Delta(O) = -0.4$. It may be concluded from this simplified picture that the bonds in these tetrahedral complexes are polarized and that the degree of polarization seems to be rather similar.

The present calculations deal entirely with the thermodynamic stability of ArO_4 in comparison with its *isoelectronic* analogues. A quantitative study of the kinetic stability or possible dissociation pathways of the ArO_4 complex would be much more demanding since it requires the determination of major parts of the multidimensional potential hypersurface. Although this is certainly an interesting question, it was not the objective of the present investigation and has to be left for future studies.

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