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A quantum-chemical study of the geometries and electronic structures of ArO and $[Ar,O,H]^+$: proton affinities of singlet and triplet ArO

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A computational study of the $[Ar,O,H]^+$ cation, a possible interference ion in ICP mass spectrometry, has been performed. Three singlets and three triplets at local minima were found. Structural optimizations were performed at MP2(full)/aug-cc-pVTZ and single-point calculations were done at these optimum geometries using CCSD(T)(full)/aug-cc-pVTZ. The lowest-energy isomer is the singlet $Ar–O–H^+$ ion **1**, isoelectronic with the hypochlorous acid. Two other singlets, $Ar--H–O^+$ and $H–Ar^+--O$, are higher in energy by 57.5 and 85.7 kcal mol^{-1}, respectively. The low-energy triplets are $Ar--H–O^+$ (0.2 kcal mol^{-1} above **1**) and $Ar--OH^+$ (2.3 kcal mol^{-1} above **1**). The third triplet, $H–Ar^+--O$, is 33.4 kcal mol^{-1} above **1**. The computed proton affinities of ArO in its singlet and triplet states are 174.1 and 129.9 kcal mol^{-1}, respectively. The deprotonation energy of the singlet $ArOH^+$ **1** strongly depends on the change in multiplicity: 174.1 kcal mol^{-1} forming singlet ArO, and 130.1 kcal mol^{-1} forming the triplet. Deprotonation energies of the two low-energy triplets $Ar--H–O^+$ and $Ar--OH^+$ are 129.9 and 127.8 kcal mol^{-1}, respectively.

1. Introduction

The chemistry of noble gases is a fascinating topic from a fundamental point of view. Covalently bound compounds of krypton, xenon and radon have been prepared.[1–3] Argon, as well as neon and helium, forms only clathrates in the condensed phase.[2,3] The observed gas-phase compounds of Ar are more diverse: binary cations such as ArH^+,[4,5] ArN^+,[4–6] ArO^+ [4,5,7,8] and ArF^+,[9] neutral van der Waals complexes such as $Ar--O$ [10,11] and $Ar--OH$,[12,13] and cluster ions such as Ar_nO^+, $Ar_n(O_2)^+$,[14] $Ar_m(O_2)_n^-$ and $Ar_m(O_2)_nO^-$.[15,16] Quantum-chemical calculations on binary Ar-containing cations have been performed[5,17–20] and their results indicate that ArX^+ ions with electronegative elements (X = N, O, F, Cl) can be divided into two groups. Cations of the first group are formed between Ar and atomic ions X^+ having an empty valence orbital which allows formation of a strong and short donor–acceptor bond $Ar \rightarrow X^+$. ArN^+ ($^3\Sigma^-$), ArF^+ ($^1\Sigma^+$), and $ArCl^+$ ($^1\Sigma^+$), all in their ground states, and excited ArO^+ ($^2\Pi$) cations[17,19] belong to this first group. The second group consists of more weakly bound complexes of Ar with ions X^+ that have no empty valence orbitals. These include ArO^+ in its ground state ($^4\Sigma^-$), and ArF^+ and $ArCl^+$ cations in excited state configurations ($^3\Pi$).[17,19]

The present work has been undertaken in order to expand knowledge of the gas-phase chemistry of argon and to include the $[Ar,O,H]^+$ system in the list of investigated Ar-containing species. This system is of interest both from a fundamental point of view and in inductively coupled plasma (ICP) mass-spectrometry since Ar is frequently used in plasma generators.[21,22] The $m/z = 57$ peak in the mass spectra of water-containing Ar plasma has been attributed to the $[Ar,O,H]^+$ ion.[22,23] To our knowledge, there have been no reports of calculations dealing with the $[Ar,O,H]^+$ ion. In the present work, we examine the $[Ar,O,H]^+$ potential energy surface, and compute the proton affinity of ArO and deprotonation energy of $[Ar,O,H]^+$.

2. Details of computations

Calculations were performed using the GAUSSIAN 98 program.[24] The natural charges[25] were computed with the NBO program[26] incorporated in GAUSSIAN 98. The Dunning correlation-consistent triple-zeta basis set augmented with the diffuse functions, aug-cc-pVTZ,[27] was used in the calculations.

Geometric parameters of the species involved were optimized at RMP2(full) (for singlets) and at UMP2(full) (for triplets) levels.[28] It is known[29–31] that spin-unrestricted (UMP2) calculations may lead to inaccurate geometries in cases of large spin contamination. However, in the ions studied here the spin contamination was moderate (S^2 did not exceed 2.018, *vs.* ideal 2.0) in all the triplet species considered. As a check of the validity of UMP2 geometries, we performed spin-restricted (ROMP2) calculations for the triplet ArO and isomers of $[Ar,O,H]^+$. The UMP2 and ROMP2 geometries for these species were found to be close (maximum deviation 0.034 Å for bond lengths and 1.4° for valence angles). Therefore, we chose to use the former for the sake of consistency for the single-point CCSD(T) calculations (the latter may be performed by GAUSSIAN 98 only within the spin-unrestricted formalism). All optimized structures were characterized by harmonic frequency calculations. The one transition state located was checked using the IRC method.[32] Final energies were computed at the CCSD(T)(full) level and corrected for the zero-point and thermal energies obtained from the MP2 frequency calculations.

The basis set superposition errors (BSSE)[33] were computed for the energies of weak bonds (<15 kcal mol^{-1}), but not included in the energy diagram. Instead, we present both the uncorrected and BSSE-corrected energies of the weak bonds in the discussion.

3. Results and discussion

In order to find the lowest energy form of $[Ar,O,H]^+$, we

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examined both the singlet and triplet potential energy surfaces (PES) of this cation. The singlet PES was chosen, as it should contain the closed shell Ar^+–O–H molecule, while the triplet PES should involve complexes of Ar with the lowest-energy triplet state[34] of the OH^+ cation. Below we will describe the singlet and triplet PES of $[Ar,O,H]^+$, then the ArO molecule, and finally compute proton affinities of ArO and deprotonation energies of $[Ar,O,H]^+$ dependent on the spin states of reactants and products.

3.1. Singlet potential energy surface of $[Ar,O,H]^+$

Structures at three local minima on the singlet $[Ar,O,H]^+$ potential energy surface were found. Their geometric parameters are presented in Fig. 1, and their relative energies given in Fig. 2. The calculated energies are given in Table 1. The lowest energy isomer **1** has an Ar–O–H connectivity. The positive charge is shared between the argon (+0.77 *e*) and hydrogen (+0.55 *e*) atoms, whereas the central oxygen is negative (−0.32 *e*). The charge on the argon atom in **1** is very different from that in all other isomers (**2**, **4**, **5**) composed of the Ar and OH fragments for which no more than +0.15 *e* resides on Ar. The Ar–O bond in **1** (1.684 Å) is the shortest amongst all the $[Ar,O,H]^+$ isomers, notably much shorter than in the triplet of the Ar–O–H connectivity (structure **4**, 2.352 Å). The computed binding enthalpy of the Ar–O bond is 71.1 kcal mol^{-1}. **1** is isoelectronic and structurally similar to hypochlorous acid, ClOH. Indeed, the computed structural parameters for **1** ($r_{Ar–O}$ = 1.684 Å, $r_{O–H}$ = 0.987 Å, ∠ArOH = 102.0°) are very close to the corresponding parameters for ClOH that we computed at MP2(full)/Aug-cc-pVTZ ($r_{Cl–O}$ = 1.692 Å, $r_{O–H}$ = 0.966 Å, ∠ClOH = 102.7°). The experimental (spectroscopic) values for ClOH[35] are $r_{Cl–O}$ = 1.689 Å, $r_{O–H}$ = 0.964 Å and ∠ClOH = 103.0°.

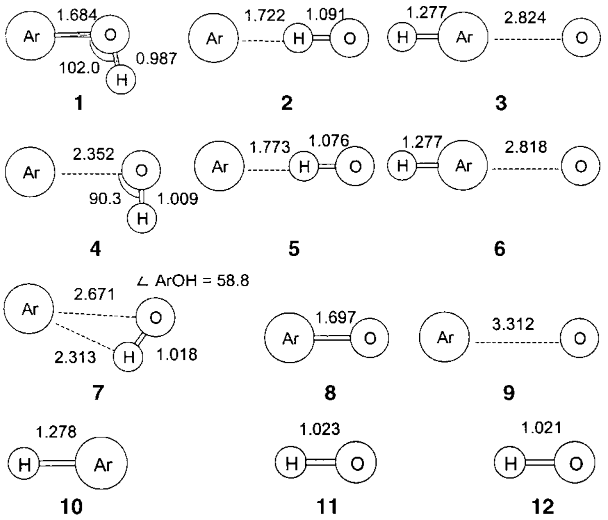

Fig. 1 Geometric parameters determined at MP2(full)/aug-cc-pVTZ. Distances are in ångstroms and angles in degrees.

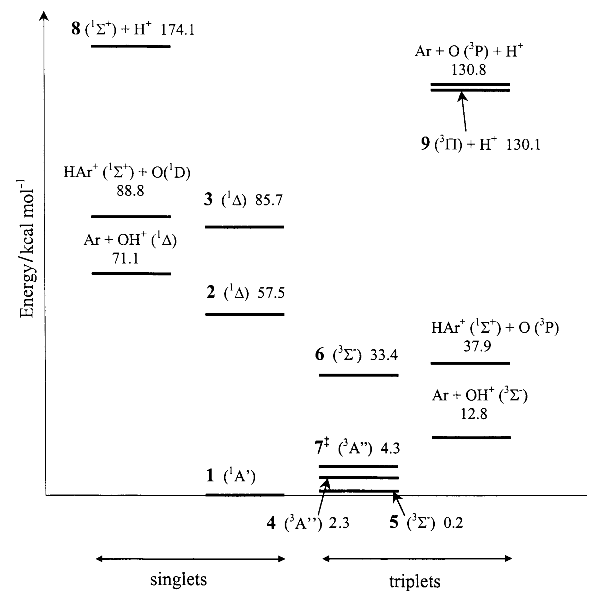

Fig. 2 Calculated relative enthalpies, in kcal mol^{-1}, of the $[Ar,O,H]^+$ structural isomers in their singlet and triplet states at 298 K. The calculations were performed at the CCSD(T)(full)/aug-cc-pVTZ//(U)MP2(full)/aug-cc-pVTZ level of theory.

Another singlet local minimum **2**, computed in this study, has an Ar–H–O connectivity and can be considered as an OH^+ singlet cation, hydrogen-bonded to the argon atom. The strength of this hydrogen bond is 13.6 kcal mol^{-1} (BSSE-corrected 11.4 kcal mol^{-1}). The positive charge of **2** is mainly located on the OH fragment (+0.39 *e* on O and +0.46 *e* on H), with only a small portion (+0.15 *e*) residing on Ar. Ion **2** is computed to be much (57.5 kcal mol^{-1}) higher in energy than **1**.

Finally, a singlet cation with an H–Ar–O connectivity was found (**3**). Cation **3** is very high in energy (85.7 kcal mol^{-1} above **1**) and can be considered as a van der Waals complex of the HAr^+ ion with a singlet oxygen atom, as seen from the long (2.824 Å) and weak Ar--O bond (3.1 kcal mol^{-1}, BSSE-corrected 2.6 kcal mol^{-1}). The positive charge of **3** resides almost totally on hydrogen (+0.49 *e*) and argon (+0.51 *e*), with the positive charge on oxygen being smaller than 0.01 *e*.

Table 1 Total PMP2(full)/aug-cc-pVTZ and CCSD(T)(full)/aug-cc-pVTZ energies (E_e) of the investigated compounds in E_h, computed with the (U)MP2(full)/aug-cc-pVTZ geometries

Species	E_e(PMP2(full))	E_e(CCSD(T)(full))	ZPE	ZPE + E_t + PV
$Ar–OH^+$ ($^1A'$) (**1**)	−602.246 831	−602.288 775	0.012 981	0.016 858
$Ar--HO^+$ ($^1\Delta$) (**2**)	−602.126 567	−602.192 499	0.008 235	0.012 293
$H–Ar–O^+$ ($^1\Delta$) (**3**)	−602.079 793	−602.148 073	0.007 602	0.012 648
$Ar--OH^+$ ($^3A''$) (**4**)	−602.235 583	−602.282 063	0.009 315	0.013 843
$Ar--HO^+$ ($^3\Sigma^-$) (**5**)	−602.242 387	−602.284 251	0.008 657	0.012 717
$H–Ar–O^+$ ($^3\Sigma^-$) (**6**)	−602.187 782	−602.231 285	0.007 672	0.012 668
TS ($^3A''$) (**7**‡)	−602.233 539	−602.277 130	0.007 884	0.012 163
Ar–O ($^1\Sigma^+$) (**8**)	−601.957 803	−602.001 618	0.001 354	0.004 822
Ar--O ($^3\Pi$) (**9**)	−602.030 634	−602.071 272	0.000 105	0.004 253
ArH^+ ($^1\Sigma^+$) (**10**)	−527.207 439	−27.233 136	0.006 273	0.009 578
OH^+ ($^1\Delta$) (**11**)	75.047 677	−75.091 264	0.007 288	0.010 593
OH^+ ($^3\Sigma^-$) (**12**)	−75.165 630	−75.184 314	0.007 334	0.010 639
Ar (^1S)	−527.057 374	−527.080 283	0	0.002 360
O (^1D)	−74.865 461	−74.909 152	0	0.002 360
O (^3P)	−74.972 667	−74.990 351	0	0.002 360

Zero-point energies (ZPE) and thermal corrections to enthalpies at 298 K (E_t + PV) in E_h, computed at (U)MP2(full)/aug-cc-pVTZ.

3.2. Triplet potential energy surface of $[\mathrm{Ar,O,H}]^+$

We also located three structures at local minima on the triplet $[\mathrm{Ar,O,H}]^+$ potential energy surface. Isomer **4** has the same connectivity as singlet **1**, but has a much longer Ar–O distance (2.352 *vs.* 1.684 Å) and a charge distribution dissimilar to **1**. Indeed, the positive charge of **4** is located mainly on the OH group (+0.41 *e* on O and +0.50 *e* on H), indicating that this structure is a van der Waals complex of triplet OH^+ cation with Ar. The computed argon binding energy is 10.5 kcal mol^{-1} (BSSE-corrected 9.5 kcal mol^{-1}). The value of the Ar–O–H angle in **4** (90.3°) indicates that the argon atom interacts mainly with one of the singly occupied p-orbitals of the oxygen. Structure **4** is 2.3 kcal mol^{-1} higher in energy than **1**.

Isomer **5** is another complex of the triplet OH^+ cation with Ar, the two subunits being connected through a hydrogen bond. As in **4**, the positive charge in **5** is mainly located on the OH group (+0.42 *e* on O and +0.45 *e* on H). The argon binding energy in **5** is 12.6 kcal mol^{-1} (BSSE-corrected 10.6 kcal mol^{-1}), and the total energy of **5** is only slightly (0.2 kcal mol^{-1}) higher than that of **1**.

A transition state for transformation of **4** into **5** has been located (**7**‡). The computed activation energy for OH^+ rotation in **4** is only 2.0 kcal mol^{-1}.

The third triplet isomer, **6**, has an H–Ar–O connectivity and is a van der Waals complex of HAr^+ with a triplet oxygen atom. Isomer **6** is 33.4 kcal mol^{-1} higher in energy than **1**, the oxygen binding energy in **6** being 4.5 kcal mol^{-1} (BSSE-corrected 4.0 kcal mol^{-1}). The positive charge of **6** resides essentially on hydrogen (+0.49 *e*) and argon (+0.50 *e*).

In summary, we found three singlet isomers and three triplet isomers of $[\mathrm{Ar,O,H}]^+$ at local minima. Of these six isomers, singlet **1** has the lowest energy, and triplets **4** and **5** are slightly higher in energy. The remaining isomers lie much higher on the potential energy surface.

3.3. Singlet and triplet ArO

For ArO, we computed the lowest-energy singlet (**8**) and triplet (**9**) states. Triplet **9** is lower in energy and is in fact a van der Waals diatomic complex, with a long Ar–O distance (3.312 Å) and nearly zero atomic charges. The computed binding energy in this complex is only 0.7 kcal mol^{-1} (BSSE-corrected 0.5 kcal mol^{-1}). Singlet **8** is 44.0 kcal mol^{-1} above the triplet. **8** has a zwitterionic structure $Ar^+–O^-$ (the charges are +0.49 *e* on Ar and −0.49 *e* on O), and is isoelectronic with the chlorine monofluoride ClF. The computed bond lengths in **8** (1.697 Å) and in ClF (1.635 Å) are similar. The computed bond dissociation energy in **8** (forming neutral argon and neutral singlet oxygen) is 7.6 kcal mol^{-1} (BSSE-corrected 4.4 kcal mol^{-1}). This value is larger than that for triplet **9**, but much smaller than that for ClF (59.8 kcal mol^{-1}, as computed at the same level).

3.4. Proton affinity of ArO and deprotonation energy of $[\mathrm{Ar,O,H}]^+$

Now we consider the proton affinity of ArO in cases of the proton attachment to the oxygen atom, to the argon atom, or insertion between the two (Table 2). For ArO in its lowest-energy triplet state **9**, the highest proton affinity (129.9 kcal mol^{-1}) corresponds to insertion of the proton between Ar and O (yielding isomer **5**). Such an insertion is somewhat unusual, but is facilitated by the weakness of the Ar––O bond in **9**. A slightly lower value (127.8 kcal mol^{-1}) results from the protonation at oxygen (yielding **4**). Protonation at argon (yielding **6**) is much less favorable (96.7 kcal mol^{-1}). This is not surprising, given the order of proton affinities of the isolated argon and oxygen atom, 88.2 kcal mol^{-1} for Ar *vs.* 116.0 kcal mol^{-1} for O.[36]

Table 2 Enthalpy changes at 298 K (PA) for protonation of ArO in its singlet and triplet states

Neutral molecule	Protonated molecule	PA/ kcal mol^{-1}
Ar–O ($^1\Sigma^+$) (**8**)	$Ar–OH^+$ ($^1A'$) (**1**)	174.1
Ar–O ($^1\Sigma^+$) (**8**)	$Ar––HO^+$ ($^1\Delta$) (**2**)	116.6
Ar–O ($^1\Sigma^+$) (**8**)	$H–Ar–O^+$ ($^1\Delta$) (**3**)	88.4
Ar––O ($^3\Pi$) (**9**)	$Ar––OH^+$ ($^3A''$) (**4**)	127.8
Ar––O ($^3\Pi$) (**9**)	$Ar––HO^+$ ($^3\Sigma^-$) (**5**)	129.9
Ar––O ($^3\Pi$) (**9**)	$H–Ar–O^+$ ($^3\Sigma^-$) (**6**)	96.7
Ar––O ($^3\Pi$) (**9**)	$Ar–OH^+$ ($^1A'$) (**1**)	130.1

For ArO in its singlet state **8**, the highest proton affinity (174.1 kcal mol^{-1}) corresponds to protonation at oxygen (yielding isomer **1**). This large value is likely due to the large negative charge on oxygen (−0.49 *e*) in singlet ArO. Insertion of the proton between Ar and O (yielding **2**) is much less favorable (116.6 kcal mol^{-1}). Protonation at Ar (yielding **3**) is the least favorable (88.4 kcal mol^{-1}).

The calculations predict a very interesting behavior of the singlet $ArOH^+$ **1** with respect to deprotonation. Assuming no change in multiplicity, the high-energy singlet state of ArO **8** must be formed, and the deprotonation energy of **1** is high (174.1 kcal mol^{-1}). However, if deprotonation of **1** is accompanied by a change in multiplicity (*i.e.* in parallel with the corresponding change in the partner molecule, thereby preserving the total multiplicity of the system), ArO in its triplet state **9** might be formed, and the deprotonation energy is much lower (130.1 kcal mol^{-1}).

Deprotonation of triplet $[\mathrm{Ar,O,H}]^+$ isomers **4** and **5** does not require a change in multiplicity to produce ArO in its lowest-energy triplet state **9**. The computed deprotonation energies are 127.8 and 129.9 kcal mol^{-1} for **4** and **5**, respectively.

4. Conclusions

We have performed a computational study of the $[\mathrm{Ar,O,H}]^+$ cation, a possible interference ion in ICP mass-spectrometry. The potential energy surfaces of $[\mathrm{Ar,O,H}]^+$ in its singlet and triplet states have been systematically examined. Three singlets and three triplets at local minima were found. The lowest-energy isomer is the singlet $Ar–O–H^+$ ion **1**, isoelectronic with hypochlorous acid. Two other singlets, $Ar––H–O^+$ and $H–Ar^+––O$, are higher in energy by 57.5 and 85.7 kcal mol^{-1}, respectively. The low-energy triplets are $Ar––H–O^+$ (0.2 kcal mol^{-1} above **1**) and $Ar––OH^+$ (2.3 kcal mol^{-1} above **1**). The third triplet, $H–Ar^+––O$, is 33.4 kcal mol^{-1} above **1**.

Our study has revealed several special features of the $[\mathrm{Ar,O,H}]^+$ potential energy surface. First, a strong (71.1 kcal mol^{-1}) Ar–O bond and a high (+0.77 *e*) positive charge on Ar in the lowest-energy isomer **1** is predicted. Second, the lowest-energy singlet and triplet isomers are found to have very similar energies. Third, the most thermochemically favorable protonation of ArO in its triplet state is through insertion of the proton between Ar and O.

The fourth special feature of the $[\mathrm{Ar,O,H}]^+$ potential energy surface is the strong dependence of the deprotonation enthalpy of **1** on the change in multiplicity. The computed deprotonation energy is 174.1 kcal mol^{-1} without change in multiplicity, and much lower (130.1 kcal mol^{-1}) for the case when deprotonation is accompanied by the change in multiplicity.

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