First compounds with argon–carbon and argon–silicon chemical bonds

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Argon is one of the three most chemically inert elements in nature, neon and helium being the other two. Only a single chemically bound, neutral compound of Ar is experimentally known to date: HArF.1 While all noble gas elements are chemically inert, there is a qualitative difference between the heavier rare gases and Ar, Ne, He. For krypton and xenon, a substantial range of compounds have been prepared.2–11 By previous theoretical calculations, two chemically bound compounds of the lighter rare gases are predicted to exist in addition to HArF (Refs. 1, 12–15), being HArCl (Refs. 6, 16, 17) and HHeF (Refs. 13, 18–21). The results of the present paper show, however, that the chemistry of argon is far richer than hitherto suspected. Two chemically bound compounds of Ar are predicted here, FArCCH and FArSiF3. The nature of the chemical bonds in these molecules is substantially different than in HArF, and they are considerably more stable than HArF. Moreover, the structure of these molecules, and the nature of Ar–Si and Ar–C bonds suggest that these are prototypes of two large families of argon-containing compounds.

The investigation of the new molecules was carried out as follows: First, a search was made for the existence of a local minimum on the potential energy surface that should correspond to the predicted species. This was done by ab initio electronic structure methods such as MP2 and CCSD(T), using the code packages GAMESS22 and GAUSSIAN.23 The most extensively employed algorithm was MP2 = full/aug-cc-pvDZ.22 Next, again using ab initio codes, the vibrational frequencies of the species were computed in the harmonic approximation. This provides important clues on the expected stability. A very soft vibrational frequency indicates possible instability. When all computed frequencies of a polyatomic species are relatively high, the compound is likely to be stable. The vibrational frequencies are extremely useful in the spectroscopic identification of matrix isolated species. Next, energy differences between the predicted compound and related species (e.g., decomposition products of the molecule) were computed. The compounds predicted here are metastable, as are indeed most rare gas compounds. Nevertheless, energetic differences with regard to other, related species are very useful data for preparation strategies. Finally, barriers for decomposition channels of the predicted species were calculated, and the energy along the minimum energy path for decomposition was explored. These properties are extremely helpful in assessing the stability of the compounds in conditions where kinetic considerations dominate. The goal is obviously to find compounds protected by high energy barriers. Such compounds, once prepared, can be stable experimentally for indefinitely long times even when their decomposition is highly exoergic.15,20 Methods such as MP2, which are single-reference, are generally not valid far from the equilibrium configurations of the species.15 Generally, multireference methods must be used in the exploration of the decomposition pathways. The MCQDPT method from GAMESS22,24 was employed here for this purpose.

FArCCH: The motivation to study the species came from the properties of HXeCCH, the existence of which was predicted by the authors.25 The latter compound and HKr–CCH were most recently experimentally prepared.26-28 The geometry of FArCCH, and the electronic charge distribution as computed by MP2 = full/aug-cc-pvDZ,22 is shown in Fig. 1. Higher level CCSD(T) calculations for the geometry and frequencies were also carried out, with very similar results. The short F–Ar and Ar–C distances, 1.92 Å and 1.86 Å, respectively, are a first indication of strong chemical bonding. The C–C and C–H distances are similar to those in acetylene. The partial charges on the atoms (in a.u., computed by the NBO approach23 are −0.579 for F, +0.685 for Ar, −0.119 and −0.236 for the first and the second carbon,
respective, and +0.249 for the H. The results show that the extremely stable, closed outermost electronic shell of isolated Ar is opened in the bonding, and that substantial negative charge is transferred to the F and the CC group. Essential to the formation of the bond is that the CC group accepts a substantial fraction of the charge transferred from the Ar. The negative charge receiving property of CC plays also a key role in the stability of HXeCCH.\textsuperscript{25} The CC bond is found to be somewhere between a double and a triple one, though nearer to the latter. The electron charge density contours in Fig. 1 indicate that there is at least some covalent bonding between Ar and CC, in addition to the major ionic contribution. The covalent contribution to the binding is estimated to be about 25%. The harmonic frequencies of normal mode vibrations of FArCCH are given in Table I. The vibrational frequencies are relatively high, as characteristic of stable, chemically bound molecules. Instability associated with a soft vibrational mode is ruled out. FArCCH is by 5.5 eV less chemically bound molecules. If there is no barrier, and MP2 gives a barrier of 1.46 eV. The potential along the minimum energy path for FArCCH is shown in Fig. 2. We used Hartree–Fock calculations to roughly estimate barriers for other decomposition pathways. The barrier is 4.6 eV for FArCCH→F+Ar+CCH, and 3.0 eV for FArCCH→Ar+C₂+HF. These barriers indicate high kinetic stability of FArCCH against decomposition. Derivatives FArCCR of FArCCH, e.g., for R that is a hydrocarbon radical group are expected to be of stability roughly similar to that of FArCCH. Preliminary results of calculations by the authors support this expectation. Thus, FArCCH is a gateway to a whole family of molecules, to organo-argon chemistry. The question of a preparation strategy for FArCCH is obviously of great interest. The most recent preparations of HXeCCH (Refs. 26, 27) and of HKrCCH (Ref. 28), using photodissociation or fast-electron dissociation of a molecule in the rare-gas matrix, are very encouraging for such an approach.

**FArSiF\textsubscript{3}:** To our knowledge, there are no experimentally known molecules with a rare-gas–silicon bond. One compound, FXeSiF, was theoretically predicted.\textsuperscript{29} The geometry and electronic charge density distribution of FArSiF\textsubscript{3} are shown in Fig. 3. The short bond distances are consistent with a chemically bound molecule. The partial charges are (in a.u.): −0.834 on F; +0.357 on Ar; +2.373 on Si and −0.632 on each F atom bound to Si. The F–Ar bond is mostly ionic, as seen from the charge distribution. However, there is a substantial covalent contribution (about 50%) to the Ar–Si bond. The vibrational frequencies, shown in Table II, are high for a molecule of such heavy atoms. The values indicate the species is fairly stable. FArSiF\textsubscript{3} is much higher in energy (6.7 eV) than Ar+SiF\textsubscript{4}. The compound is more stable by 0.05 eV than F+Ar+SiF\textsubscript{3}. Equilibrium considerations are thus very unfavorable for the existence of the compound. However, the kinetic stability of the compound is quite high, ample for its existence (once prepared) in cryogenic conditions: the barrier for FArSiF\textsubscript{3}→Ar+SiF\textsubscript{4}, computed by MP2, is 0.41 eV, and the barrier for FArSiF\textsubscript{3}→F+Ar+SiF\textsubscript{4}, computed by the multireference method MCQDPT\textsubscript{2} (Ref. 22) is 0.47 eV.

For FArSiF\textsubscript{3}, as for FArCCH, obvious possibilities of derivatives exist. A possible family of derivatives is FArSiF\textsubscript{2}Y, where Y denotes a strongly electronegative

**FIG. 1.** Geometry and electronic density contours of FArCCH. Distances are in Å.

**FIG. 2.** The potential along the minimum energy path for FArCCH→Ar + FCCH.

**FIG. 3.** Geometry and electronic density contours of FArSiF\textsubscript{3}. Distances are in Å.

**TABLE I.** Harmonic frequencies of FArCCH.

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>Frequency (cm\textsuperscript{-1})</th>
</tr>
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<tbody>
<tr>
<td>C–H Stretch</td>
<td>3441.70</td>
</tr>
<tr>
<td>C–C Stretch</td>
<td>2028.49</td>
</tr>
<tr>
<td>Ar–CC–H Bend\textsuperscript{a}</td>
<td>594.14</td>
</tr>
<tr>
<td>F–Ar Stretch</td>
<td>542.82</td>
</tr>
<tr>
<td>F–Ar–C Bend\textsuperscript{a}</td>
<td>330.83</td>
</tr>
<tr>
<td>Ar–C Stretch</td>
<td>302.76</td>
</tr>
<tr>
<td>FArCCH Bend\textsuperscript{a}</td>
<td>116.40</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Degenerate mode.
group. Again, it is expected that the stability of these derivatives should be of the same order as FArSiF$_3$. There are thus encouraging prospects for silicon–argon chemistry. A preparation strategy based on photochemistry in a low-temperature argon matrix seems natural to attempt also in this case. In summary, the compounds predicted here, with carbon–argon and silicon–argon bonds, respectively, seem to suggest the existence of argon chemistry as a substantial field. At present, the heavy rare-gas elements have a wide range of compounds, while for Ar, Ne, and He, not even a handful of chemically bound molecules have been predicted. It seems conceivable, however, that a rich chemistry of the light rare-gases will emerge soon.

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