

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/238656672>

# Generation of the ArCF 2 2+ Dication

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JANUARY 2010

Impact Factor: 7.46 · DOI: 10.1021/jz900274p

CITATIONS

29

READS

18

## 9 AUTHORS, INCLUDING:



[Małgorzata Karwowska](#)

University of Warsaw

2 PUBLICATIONS 56 CITATIONS

[SEE PROFILE](#)



[Karol J Fijalkowski](#)

University of Warsaw

16 PUBLICATIONS 228 CITATIONS

[SEE PROFILE](#)



[Marek Remeš](#)

University of Münster

8 PUBLICATIONS 90 CITATIONS

[SEE PROFILE](#)



[Jana Roithová](#)

Charles University in Prague

154 PUBLICATIONS 2,870 CITATIONS

[SEE PROFILE](#)

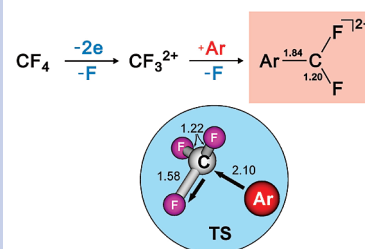
# Generation of the $\text{ArCF}_2^{2+}$ Dication

Jessica F. Lockyear,<sup>†</sup> Kevin Douglas,<sup>†</sup> Stephen D. Price,<sup>†</sup> Małgorzata Karwowska,<sup>‡</sup> Karol J. Fijalkowski,<sup>‡</sup> Wojciech Grochala,<sup>‡,§</sup> Marek Remeš,<sup>#,⊥</sup> Jana Roithová,<sup>#,⊥</sup> and Detlef Schröder<sup>\*,⊥</sup>

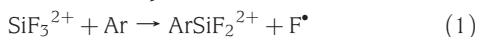
<sup>†</sup>Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom, <sup>‡</sup>Faculty of Chemistry, University of Warsaw, Pasteur 1, 02093 Warsaw, Poland, <sup>§</sup>University of Warsaw, ICM, Pawinskiego 5a, 02106 Warsaw, Poland, <sup>#</sup>Department of Organic and Nuclear Chemistry, Faculty of Sciences, Charles University in Prague, 12843 Prague 2, Czech Republic, and <sup>⊥</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

**ABSTRACT** Thermal reactions of the  $\text{CF}_3^{2+}$  dication with argon lead to the formation of an  $\text{ArCF}_2^{2+}$  dication, a new type of metastable species with an argon–carbon bond. None of the other rare gases undergo a similar reaction with  $\text{CF}_3^{2+}$ . For the lighter rare gases (He and Ne), no reactions with  $\text{CF}_3^{2+}$  other than those due to electronically excited reactant ions are observed, whereas for the heavier rare gases (Kr and Xe), the prevailing reactive pathways involve single-electron transfer. At elevated collision energies, single-electron transfer predominates for collisions with all rare gases (He–Xe).

**SECTION** Molecular Structure, Quantum Chemistry, General Theory



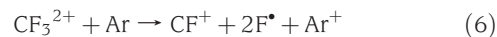
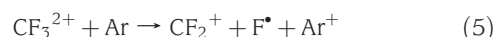
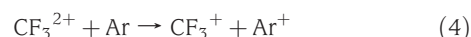
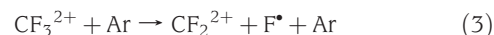
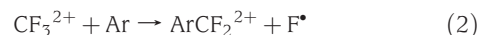
The formation of rare-gas compounds, first discovered in 1962,<sup>1</sup> is an attractive field for chemical research, which recently experienced additional stimuli by the photochemical generation of several new rare-gas compounds in matrix isolation experiments.<sup>2–4</sup>



Inspired by the recent observation of the gaseous dication  $\text{ArSiF}_2^{2+}$ , having an argon–silicon bond, formed in thermal collisions of the mass-selected  $\text{SiF}_3^{2+}$  dication with argon (reaction 1),<sup>5</sup> we decided to follow an earlier prediction that halocarbene dications should also form reasonably stable adducts with rare gases.<sup>6</sup> In this context, an important conclusion from the investigation of reaction 1 was that the chances for the successful observation of bond-forming reactions of molecular dications<sup>7,8</sup> are particularly large at low collision energies, preferentially, in the thermal regime. For example, earlier studies of  $\text{SiF}_3^{2+} + \text{Ar}$  failed to observe reaction 1 due to the elevated experimental collision energies.<sup>9</sup> Accordingly, we felt it worthwhile to reinvestigate the analogous low-energy collisions of the  $\text{CF}_3^{2+}$  dication with the rare gases He–Xe. The reactions of  $\text{CF}_3^{2+}$  with the rare gases have been the subject of several previous investigations at elevated (few eV) collision energies,<sup>10,11</sup> as have the reactions of  $\text{CF}_3^{2+}$  with deuterium molecules.<sup>12,13</sup>

The  $\text{CF}_3^{2+}$  dication can be easily generated by (dissociative) double ionization of tetrafluoromethane with energetic electrons or photons.<sup>14–16</sup> It has a very high single-electron recombination energy to form  $\text{CF}_3^+$ ,  $\text{RE}(\text{CF}_3^{2+}) = 26.3 \text{ eV}$ ,<sup>17,18</sup> and a weak C–F bond,  $D(\text{F}_2\text{C}^{2+}-\text{F}) = (1.1 \pm 0.4) \text{ eV}$ ,<sup>14,19,20</sup> which can be attributed to the presence of a localized hole in the  $\sigma$ -bonding C–F orbital. Accordingly, in bimolecular encounters, more strongly bonding substituents

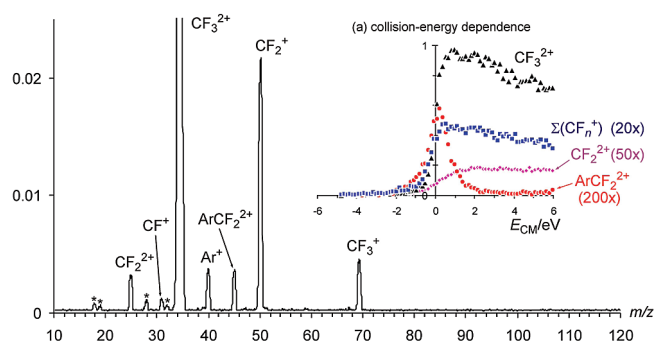
might be induced to replace this weakly bound fluorine atom as we have recently demonstrated for the reactions of the heavier analogue  $\text{SiF}_3^{2+}$ .<sup>5,21</sup>



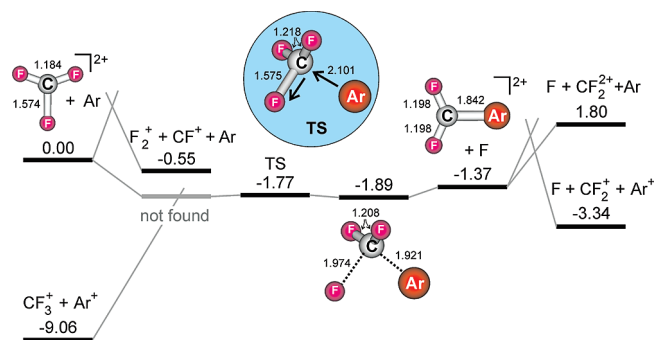
Our experiments reveal that the interaction of mass-selected  $\text{CF}_3^{2+}$  with neutral argon generates  $\text{ArCF}_2^{2+}$  formed via the substitution reaction 2. Additional processes observed (Figure 1) correspond to dication dissociation (reaction 3), either collision-induced or arising from metastable states, and charge separations according to reactions 4–6, of which the latter has previously been assigned to an excited state of  $\text{CF}_3^{2+}$ .<sup>10</sup> Reactions 3, 5, and 6 have been clearly observed before at collision energies of 1.8 and 4.4 eV, and weak contributions from reaction 4 can be traced at a collision energy of 3.0 eV.<sup>11</sup> However, the  $\text{ArCF}_2^{2+}$  product and strong signals due to  $\text{CF}_3^+$ , reactions 2 and 4, are only observed following the low-energy collisions studied in this work. This increase in the  $\text{ArCF}_2^{2+}$  signals at low collision energy is demonstrated by the energy dependence of the  $\text{ArCF}_2^{2+}$

**Received Date:** November 16, 2009

**Accepted Date:** December 2, 2009



**Figure 1.** Reaction of mass-selected  $CF_3^{2+}$  dications with argon at an octopole voltage of  $U_{oct} = -2$  V and  $p(Ar) = 2 \times 10^{-4}$  mbar; these conditions correspond to a nominal laboratory energy of reactant ions set close to zero. The vertical scale refers to the precursor dication with an intensity of 1.00 (off-scale). The signals denoted with asterisks are due to reactions with background moisture and air (i.e.,  $H_2O^+$ ,  $H_3O^+$ ,  $N_2^+$ , and  $O_2^+$ ). Inset (a) shows the energy dependences of the major channels in the center-of-mass scale. Note that the sum of  $CF_n^+$  monocations is shown for the sake of clarity in the graph; also, the  $Ar^+$  trace is omitted.



**Figure 2.** Minima on the potential energy surface of the  $CF_3^{2+}$  dication reacting with argon according to B3LYP/6-311+G(2d,p) calculations and a representation of the bonding C–Ar orbital. Energies are expressed in eV relative to the reactant asymptote. The selected bond lengths are given in Å.

signal in inset (a) of Figure 1, which shows a sharp maximum near a nominal collision energy of 0 eV. We note in passing that Figure 1 of ref 10 taken at a collision energy of 3.3 eV shows some elevated noise at  $m/z$  45, perhaps corresponding to the  $ArCF_2^{2+}$  product, which is consistent with the energy dependence shown in Figure 1. Similarly, the yield of the  $CF_3^+$  monocation (not separately shown in the inset of Figure 1) also has a maximum at  $E_{CM} = 0$  eV with a rapid decline at elevated collision energies.

The experimental results described above are further supported by theoretical calculations using density functional theory (Figure 2). The precursor dication  $CF_3^{2+}$  has  $C_{2v}$  symmetry with two short ( $r_{CF} = 1.184$  Å) and one long ( $r_{CF} = 1.574$  Å) C–F bond; the bond dissociation energy is computed as  $D_{calc}(CF_2^{2+} - F) = 1.80$  eV and is thus somewhat larger than the experimental estimate quoted above. The initial interaction of  $CF_3^{2+}$  with neutral argon should lead to an encounter complex, but all attempts to localize this structure led to charge separation into  $CF_3^+$  and  $Ar^+$ . However, we have found a transition structure (TS,  $E_{rel} = -1.77$  eV; see inset structure in Figure 2) for the substitution of fluorine, as a

leaving group, by argon, as a nucleophile, and also located the corresponding complex of the  $ArCF_2^{2+}$  product with a fluorine atom ( $E_{rel} = -1.89$  eV). The C–Ar bond length in the transition structure amounts to 2.101 Å. The crossing between the Coulomb-repulsion potential energy curve and that of the dication/induced dipole interaction is located at  $\sim 2.35$  Å.<sup>22</sup> Hence, single-reference calculations at geometries expected for the encounter complex, that is, the C–Ar bond most probably larger than 2.3 Å, lead to the dissociation along the  $CF_3^+ - Ar^+$  coordinate, and therefore, the encounter complex cannot be localized at this level of theory.

The final product  $ArCF_2^{2+}$  is formed by the elimination of a fluorine atom from the product complex and lies 1.37 eV below the entrance channel. The C–Ar bond length in  $ArCF_2^{2+}$  is calculated to be 1.842 Å. Both the single-bond and double-bond covalent radii of Pyykkö and Atsumi predict a C–Ar distance of about 1.7 Å,<sup>23</sup> which is significantly shorter than the value found here. According to natural bond analysis, the  $\sigma$  Ar–C bond is formed by the overlap  $2p_C$  and  $3p_{Ar}$  orbitals along the axis of the bond with an occupancy of 1.98 e. This bond however is weakened by the 0.20 e occupancy of the antibonding Ar–C orbital, where predominantly the lone pairs of the fluorine atoms contribute to the Ar–C interactions. Thus, upon analysis of the bonding, we expect the Ar–C bond to be indeed slightly longer than a “typical” Ar–C  $\sigma$  bond.

A major difference between the  $CF_3^{2+}/Ar$  collision system compared with the homologous  $SiF_3^{2+}/Ar$  interaction is that, due to the much higher single-electron recombination energy (RE) of  $CF_3^{2+}$ , nondissociative electron transfer (reaction 4) as well as dissociative electron transfer (reactions 5 and 6) are much more pronounced in the  $CF_3^{2+}/Ar$  system. The competing, very exothermic electron-transfer processes to yield pairs of monocations explain the low yield of the substitution product  $ArCF_2^{2+}$ . The significant exothermicity of the electron-transfer process between  $CF_3^{2+}$  and Ar also accounts for the dominance of dissociative electron transfer with two major pathways, formation of  $CF_2^+ + F + Ar^+$  via dissociation of an energized  $CF_3^+$  product of a primary electron transfer event (reaction 5) and via the primary reaction 2 followed by the subsequent dissociation of the  $ArCF_2^{2+}$  product.<sup>10</sup> Conceptually, our results also imply that mere electrophilicity (i.e., the recombination energy) is by no means the sole criterion for a chemically useful superelectrophile in the gas phase. In this case, precisely the opposite is true; the extreme electrophilicity of  $CF_3^{2+}$  appears to lead to the suppression of bond-forming processes due to competition with single-electron transfer (particularly for the heavier rare gases; see below). For a more successful rationalization of the bond-forming processes of molecular dications, a larger set of characteristic parameters has to be considered, as recently demonstrated for the silicon analogue of the title species.<sup>5</sup>

More generally, the experimental evidence (Figure 1) in conjunction with the theoretical data (Figure 2) is clear proof for the existence of the metastable  $ArCF_2^{2+}$  dication, a new kind of organo-argon species in the gas phase.<sup>24</sup> In this context, a brief comparison to the recently studied  $SiF_3^{2+}/Ar$  system<sup>5</sup> is quite instructive. For the silicon analogue, reaction 1 is indeed the major channel at thermal energies,

**Table 1.** Product Ions and Abundances (given in % of the parent ion) Observed in the Reactions of Mass-Selected  $\text{CF}_3^{2+}$  Dications with Rare Gases at an Octopole Voltage of  $U_{\text{oct}} = -2$  V, Which Corresponds to a Nominal Laboratory Collision Energy of  $\sim 0$  eV

	$\text{RgCF}_2^{2+}$	$\text{CF}_2^{2+}$	$\text{Rg}^{+a}$	$\text{CF}^+$	$\text{CF}_2^+$	$\text{CF}_3^+$
$\text{He}^{b,c}$		0.3		< 0.1	0.4	0.3
$\text{Ne}^{b,c}$		1.6		< 0.1	0.5	0.6
$\text{Ar}^d$	0.3	0.2	0.3	0.1	2.2	0.4
Kr	— <sup>e</sup>	< 0.1	1.8	0.3	2.1	0.1
$\text{Xe}^{c,f}$		0.1	6.8	1.2	1.8	0.1

<sup>a</sup> Sum over all isotopes. <sup>b</sup> The observed products are not corrected for collisions with background gases, and for helium and neon, the charge separation yields are likely to have major contributions from this source. <sup>c</sup> Despite a careful search, no significant signals due to  $\text{RgCF}_2^{2+}$  were observed. <sup>d</sup> In addition, traces of  $\text{ArF}^+$  ( $< 0.1\%$ ) are formed. <sup>e</sup> Only for the major isotope  $^{84}\text{KrCF}_2^{2+}$  could a signal significantly above the noise level be detected. <sup>f</sup> Given the large amount of electron transfer, the single-collision regime was not strictly maintained in the case of xenon.

whereas the maximal branching of the  $\text{ArCF}_2^{2+}$  channel in the  $\text{CF}_3^{2+}/\text{Ar}$  system amounts to only about 10 % of all product channels and, hence, is only a minor pathway. However, reaction 2 is still a much more efficient process than earlier examples of argon–carbon species generated in ion/molecule collisions,  $\text{ArC}^{2+}$ ,<sup>25,26</sup>  $\text{ArCH}_2^+$ ,<sup>27</sup> and  $\text{ArC}_2\text{H}^{2+}$ .<sup>28</sup> The differences between  $\text{CF}_3^{2+}/\text{Ar}$  and  $\text{SiF}_3^{2+}/\text{Ar}$  can be ascribed to the much larger exothermicities of the charge-transfer reactions of  $\text{CF}_3^{2+}$  (RE = 26.3 eV) with argon (IE = 15.76 eV) as compared to those of  $\text{SiF}_3^{2+}$  (RE = 22.4 eV),<sup>29</sup> such that most of the transient  $\text{ArCF}_2^{2+}$  species formed in reaction 2 will rapidly undergo charge-separation reactions. Indeed, coincidence experiments of the corresponding reaction 3 gave no evidence for the formation of long-lived intermediate complexes.<sup>11</sup>

We also briefly explored the reactions of the other rare gases with mass-selected  $\text{CF}_3^{2+}$  in order to probe if other organo rare-gas bonds can be made via this approach (Table 1). Except for a very weak signal which might correspond to  $\text{KrCF}_2^{2+}$ , none of the other rare gases undergo a bond-forming process analogous to reaction 2. This observation can be rationalized by the operation of two different effects. For the heavier rare gases, electron transfer leading to charge-separation reactions is more and more favored due to the lower ionization energies of krypton (IE = 14.00 eV) and xenon (IE = 12.13 eV). This is not the case for the two lighter rare gases, helium (IE = 24.59 eV) and neon (IE = 21.56 eV), which are resistant to one-electron oxidation by  $\text{CF}_2^{2+}$ . On the other hand, helium and neon clearly do not have potential for formation of strong donor–acceptor complexes with  $\text{CF}_2^{2+}$ , as indicated by their inability to replace the fluorine atom in  $\text{CF}_3^{2+}$ . These experimental results suggest that  $D(\text{Rg}–\text{CF}_2^{2+}) < D(\text{F}_2\text{C}^{2+}–\text{F})$  for  $\text{Rg} = \text{He}$  and  $\text{Ne}$ , which may be traced to a poor overlap between the contracted ns-valence orbitals of these rare gases and the relatively diffuse sp-hybrid on carbon.

In conclusion, we have demonstrated that the open-shell molecular dication  $\text{CF}_3^{2+}$  can serve as a suitable reagent for the generation of novel gaseous rare-gas–carbon species in

thermal ion–molecule reactions. The efficiency of this super-electrophile<sup>30</sup> with respect to  $\text{Ar}–\text{C}$  bond formation is limited by the competing charge-transfer reactions. Accordingly, formation of  $\text{RgCF}_2^{2+}$  is suppressed for  $\text{Rg} = \text{Kr}$  and  $\text{Xe}$ , while the lighter rare gases  $\text{He}$  and  $\text{Ne}$  cannot serve as Lewis bases of sufficient strength toward  $\text{CF}_2^{2+}$  and consequently cannot replace the fluorine atom in the  $\text{CF}_3^{2+}$  precursor. As a result of these different effects, among all  $\text{RgCF}_2^{2+}$  species, only  $\text{ArCF}_2^{2+}$  is formed in significant yields in  $\text{CF}_3^{2+} + \text{Rg}$  collisions. In a more general sense, the present results underline the importance of low-energy collisions in attempts to understand the bimolecular reactivity of gaseous dications.<sup>7,8,31</sup>

## Experimental Methods

The experiments were performed with a TSQ Classic mass spectrometer<sup>32,33</sup> equipped with an ion source for electron ionization (EI) and an analyzer of QQQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole, serving as a collision cell, has a separate housing which limits the penetration of gases admitted to the octopole to the ultrahigh vacuum of the manifold. The kinetic energy of the ions entering the octopole can be varied, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or at elevated kinetic energies.<sup>34–37</sup> The  $\text{CF}_3^{2+}$  dications generated by EI of  $\text{CF}_4$  were mass-selected by means of the first quadrupole (Q1) at a mass resolution fully sufficient to select only dicationic species. The mass-selected dications were then reacted with rare gases admitted to the octopole at pressures of typically  $2 \times 10^{-4}$  mbar. The collision energy was adjusted by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero point of the kinetic energy scale, as well as the width of the kinetic energy distribution, was determined by means of retarding potential analysis; for the dicationic species reported here, the beam width at half-maximum amounts to  $(2.2 \pm 0.2)$  eV in the laboratory frame. The bimolecular reactions reported below were recorded at a nominal laboratory collision energy of the reactant ions close to zero, that is, at the point of inflection of the curve obtained by retarding potential analysis of the reactant,<sup>38</sup> that is,  $U_{\text{oct}} = (1.8 \pm 0.2)$  V in the present experiments. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2 at unit mass resolution. Ion abundances were determined using a Daly-type detector operating in the counting mode. Because the reactions of  $\text{CF}_3^{2+}$  with rare gases have been previously investigated in quite some detail and multipole arrangements are not ideally suited to investigate the reaction kinetics of ion/molecule reactions,<sup>39</sup> we neither convert the relative reactivities revealed by our experiments to absolute rate constants nor make corrections for the differences in the transmission of the light and heavy product ions to the detector.<sup>40</sup>

For the (spin-unrestricted) calculations, we used the density functional methodology B3LYP<sup>41–44</sup> in conjunction with a 6-311+G(2d,p) triple- $\zeta$  basis set as implemented in the Gaussian 03 suite;<sup>45</sup> BSSE was not accounted for. Frequency



analysis at the same level of theory was performed for all optimized structures in order to assign stationary points on the potential energy surface as genuine minima or transition structures, as well as to calculate zero-point vibrational energies (ZPVEs).

**SUPPORTING INFORMATION AVAILABLE** Calculated total energies and geometries as well as a NBO analysis of  $\text{ArCF}_2^{2+}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author:

\*To whom correspondence should be addressed. Fax: 00420 220 183 462. E-mail: [schroeder@uochb.cas.cz](mailto:schroeder@uochb.cas.cz).

**ACKNOWLEDGMENT** This work was supported by the Czech Academy of Sciences (Z40550506), the Grant Agency of the Czech Republic (203/09/1223), and the Ministry of Education of the Czech Republic (MSM0021620857, RP MSMT 14/63). The cooperation between London and Prague was additionally supported by a grant of the Royal Society (London). The visit of K. F. and M.K. for a summer internship with the Prague team was supported by the University of Warsaw.

## REFERENCES

- Bartlett, N. Xenon Hexafluoroplatinate(V)  $\text{Xe}^+[\text{PtF}_6]^-$ . *Proc. Chem. Soc.* **1962**, 218.
- Gerber, R. B. Formation of Novel Rare-Gas Molecules in Low-Temperature Matrices. *Annu. Rev. Phys. Chem.* **2004**, 55, 55–78.
- Grochala, W. Atypical Compounds of Gases, which have been Called 'Noble'. *Chem. Soc. Rev.* **2007**, 36, 1632–1655.
- Khriachtchev, L.; Räsänen, M.; Gerber, R. B. Noble Gas Hydrides: New Chemistry at Low Temperatures. *Acc. Chem. Res.* **2009**, 42, 183–191.
- Roithová, J.; Schröder, D. Silicon Compounds of Neon and Argon. *Angew. Chem., Int. Ed.* **2009**, 48, 8788–8790.
- Roithová, J.; Žabka, J.; Herman, Z.; Thissen, R.; Schröder, D.; Schwarz, H. Reactivity of the  $\text{CHBr}^{2+}$  Dication Toward Molecular Hydrogen. *J. Phys. Chem. A* **2006**, 110, 6447–6453.
- Price, S. D. Investigating the Gas-Phase Chemical Reactions of Molecular Dications. *Phys. Chem. Chem. Phys.* **2003**, 5, 1717–1729.
- Roithová, J.; Schröder, D. Bimolecular Reactions of Molecular Dications: Reactivity Paradigms and Bond-Forming Processes. *Phys. Chem. Chem. Phys.* **2007**, 9, 2341–2349.
- Lee, Y.-Y.; Leone, S. R.; Champkin, P.; Kaltsoyannis, N.; Price, S. D. Laser Photofragmentation and Collision-Induced Reactions of  $\text{SiF}_2^{2+}$  and  $\text{SiF}_3^{2+}$ . *J. Chem. Phys.* **1997**, 106, 7981–7994.
- Tafadar, N.; Kaltsoyannis, N.; Price, S. D. Electron-Transfer and Neutral-Loss Reactions in Collisions of  $\text{CF}_3^{2+}$  with Argon. *Int. J. Mass Spectrom.* **1999**, 192, 205–214.
- Hu, W. P.; Harper, S. M.; Price, S. D. The Dynamics and Kinematics of the Electron Transfer Reactions of  $\text{CF}_3^{2+}$  with Ar. *Mol. Phys.* **2005**, 103, 1809–1819.
- Lambert, N.; Kaltsoyannis, N.; Price, S. D.; Žabka, J.; Herman, Z. Bond-Forming Reactions of Dications with Molecules: A Computational and Experimental Study of the Mechanisms for the Formation of  $\text{HCF}_2^+$  from  $\text{CF}_3^{2+}$  and  $\text{H}_2$ . *J. Phys. Chem. A* **2006**, 110, 2898–2905.
- Tafadar, N.; Price, S. D. Bond-Forming Reactivity Between  $\text{CF}_3^{2+}$  and  $\text{H}_2/\text{D}_2$ . *Int. J. Mass Spectrom.* **2003**, 223, 547–560.
- Masuoka, T.; Okaji, A.; Kobayashi, A. Fragmentation of  $\text{CF}_4^{2+}$  Dication from Threshold to 120 eV. *Int. J. Mass Spectrom.* **2002**, 218, 11–18.
- Torres, I.; Martinez, R.; Castano, F. Electron-Impact Dissociative Ionization of Fluoromethanes  $\text{CHF}_3$  and  $\text{CF}_4$ . *J. Phys. B* **2002**, 35, 2423–2436.
- Kobayashi, A.; Okaji, A.; Masuoka, T. Dissociative Single and Double Photoionization of  $\text{CF}_4$  and Ionic Fragmentation of  $\text{CF}_4^+$  and  $\text{CF}_4^{2+}$  from 23 to 120 eV. *Chem. Phys.* **2004**, 298, 107–117.
- Proctor, C. J.; Porter, C. J.; Ast, T.; Beynon, J. H. Evidence of Long-Lived Electronically Excited-States of Some Simple Halocarbon Ions. *Int. J. Mass Spectrom. Ion Phys.* **1982**, 41, 251–263.
- Hrušák, J.; Sändig, N.; Koch, W. Structure and Stability of the  $\text{CF}_3^{2+}$  Dication. *Int. J. Mass Spectrom.* **1999**, 185–187, 701–706.
- Stephan, K.; Deutsch, H.; Märk, T. D. Absolute Partial and Total Electron-Impact Ionization Cross-Sections for  $\text{CF}_4$  from Threshold up to 180 eV. *J. Chem. Phys.* **1985**, 83, 5712–5720.
- This figure derived from the appearance energies of  $\text{CF}_3^{2+}$  and  $\text{CF}_2^{2+}$  should be taken with some caution because the absolute values in ref 14 and 19 differ by about 1 eV.
- Roithová, J.; Schwarz, H.; Schröder, D. The  $\text{SiF}_3^{2+}$  Dication: Chemistry Counts!. *Chem.—Eur. J.* **2009**, 15, 9995–9999.
- The crossing point  $R_{\text{cross}}$  has been estimated from the equation  $(1/R_{\text{cross}}) - \Delta E_{\text{ET}} = -4\alpha_{\text{Ar}}/(R_{\text{cross}})^4$ , where  $\Delta E_{\text{ET}}$  is the calculated exothermicity of electron transfer between  $\text{CF}_3^{2+}$  and Ar (9.1 eV) and the polarizability  $\alpha_{\text{Ar}}$  is taken as  $1.586 \text{ \AA}^3$ .
- (a) Pyykkö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1–118. *Chem.—Eur. J.* **2009**, 15, 186–197. (b) Pyykkö, P.; Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li–E112. *Chem.—Eur. J.* **2009**, 15, 12770–12779.
- A reviewer (and also some of the authors) raised the question of whether isolated dications generated and probed in a mass spectrometer can correctly be termed “compounds”. While the IUPAC definition of “molecular entities” (<http://goldbook.iupac.org/M03986.html>) explicitly includes isolated ions, we have decided not to use this term in referring to species such as  $\text{ArCF}_2^{2+}$ .
- Tosi, P.; Lu, W. Y.; Correale, R.; Bassi, D. Production of the Molecular Dication  $\text{ArC}^{2+}$  by Ion–Molecule Reactions. *Chem. Phys. Lett.* **1999**, 310, 180–182.
- Lu, W. Y.; Tosi, P.; Bassi, D. Bond-Forming Reactions of Molecular Dications with Rare Gas Atoms: Production of  $\text{ArC}^{2+}$  in the Reaction  $\text{CO}^{2+} + \text{Ar}$ . *J. Chem. Phys.* **2000**, 112, 4648–4651.
- Ascenzi, D.; Tosi, P.; Roithová, J.; Schröder, D. Gas-Phase Synthesis of the Rare-Gas Carbene Cation  $\text{ArCH}_2^+$  Using Doubly Ionised Bromomethane as a Superelectrophilic Reagent. *Chem. Commun.* **2008**, 4055–4057.
- Ascenzi, D.; Tosi, P.; Roithová, J.; Ricketts, C. L.; Schröder, D.; Lockyear, J. F.; Parkes, M. A.; Price, S. D. Generation of the Organo-Rare Gas Dications  $\text{HCCRG}^{2+}$  ( $\text{Rg} = \text{Ar}$  and  $\text{Kr}$ ) in the Reactions of Acetylene Dications with Rare Gases. *Phys. Chem. Chem. Phys.* **2008**, 10, 7121–7128.
- Champkin, P.; Kaltsoyannis, N.; Price, S. D. A Theoretical Investigation of the Electron-Transfer Reactions of the  $\text{SiF}_3^{2+}$

- Dication with the Rare Gases Neon, Argon, Krypton and Xenon. *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 57–69.
- (30) Olah, G. A.; Klumpp, D. A. *Superelectrophiles and Their Chemistry*; Wiley: Hoboken, NJ, 2007.
- (31) Roithová, J.; Schröder, D. Bond-Forming Reactions of Molecular Dications as a New Route to Polyaromatic Hydrocarbons. *J. Am. Chem. Soc.* **2006**, *128*, 4208–4209.
- (32) Roithová, J.; Schröder, D. Bond-Forming Reactions Versus Electron Transfer: C–C-Coupling Reactions of Hydrocarbon Dications with Benzene. *Phys. Chem. Chem. Phys.* **2007**, *9*, 731–738.
- (33) Roithová, J.; Schröder, D.; Mišek, J.; Stará, I. G.; Starý, I. Chiral Superbases: The Proton Affinities of 1- and 2-Aza[6]helicene in the Gas Phase. *J. Mass Spectrom.* **2007**, *42*, 1233–1237.
- (34) Schröder, D.; Schwarz, H.; Schenk, S.; Anders, E. A Gas-Phase Reaction as a Functional Model for the Activation of Carbon Dioxide by Carbonic Anhydrase. *Angew. Chem., Int. Ed.* **2003**, *42*, 5087–5090.
- (35) Feyel, S.; Schröder, D.; Schwarz, H. Gas-Phase Oxidation of Isomeric Butenes and Small Alkanes by Vanadium-Oxide and -Hydroxide Cluster Cations. *J. Phys. Chem. A* **2006**, *110*, 2647–2654.
- (36) Schröder, D.; Engeser, M.; Schwarz, H.; Rosenthal, E. C. E.; Döbler, J.; Sauer, J. Degradation of Ionized  $\text{OV}(\text{OCH}_3)_3$  in the Gas Phase. From the Neutral Compound All the Way down to the Quasi-terminal Fragments  $\text{VO}^+$  and  $\text{VOH}$ . *Inorg. Chem.* **2006**, *45*, 6235–6245.
- (37) Schröder, D.; Roithová, J.; Schwarz, H. Electrospray Ionization as a Convenient New Method for the Generation of Catalytically Active Iron-Oxide Ions in the Gas Phase. *Int. J. Mass Spectrom.* **2006**, *254*, 197–201.
- (38) Herman, Z. Dynamics of Charge Transfer and Chemical Reactions of Doubly-Charged Ions at Low Collision Energies. *Int. Rev. Phys. Chem.* **1996**, *15*, 299–324.
- (39) Jagoda-Cwiklik, B.; Jungwirth, P.; Rulišek, L.; Milko, P.; Roithová, J.; Lemaire, J.; Maitre, P.; Ortega, J. M.; Schröder, D. Micro-Hydration of the  $\text{MgNO}_3^+$  Cation in the Gas Phase. *ChemPhysChem* **2007**, *8*, 1629–1639.
- (40) Ricketts, C. L.; Schröder, D.; Roithová, J.; Schwarz, H.; Thissen, R.; Dutuit, O.; Žabka, J.; Herman, Z.; Price, S. D. Competition of Electron Transfer, Dissociation, and Bond-Forming Processes in the Reaction of the  $\text{CO}_2^{2+}$  Dication with Neutral  $\text{CO}_2$ . *Phys. Chem. Chem. Phys.* **2008**, *10*, 5135–5143.
- (41) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin-Density Calculations — A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (42) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formulation into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (43) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (44) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation-Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- (45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.