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Reply to R.E. March

We wish to respond to Professor March's comments on our recent article on double electron-transfer ionization [1].

First, it is perhaps unfortunate that our article's title did not include the caveat 'under thermal collision energy ($T \sim 300$ K) conditions'. The liberation of electrons from collisions at very high kinetic energy, such as March describes, is well-accepted and has been observed in many studies. Indeed, there are several examples within the literature which already describe the production of multiply charged fullerenes in high-energy collisions with electrons and with atomic ions. For example, Schlathölter et al. [2] have described experiments in which He^+ and He^{2+} projectiles at high velocity (several keV kinetic energy) collide with C_{60}, yielding, respectively, fullerene cations in charge states up to ${C_{60}}^{3+}$ and ${C_{60}}^{5+}$. Process (1), which appears to have

$$He^{2+} + C_{60} \rightarrow He + {C_{60}}^{3+} + e \quad (1)$$

occurred in the study by Schathölter et al. [2] (although there is no evidence presented that the α-particle projectile does indeed accept two of the electrons shed by the fullerene upon impact), conforms to our process of double electron-transfer ionization (DETI), and is certainly energetically feasible, even under thermal collision energy conditions (which were not accessible in their experiment). While dications and even monocations can, with reasonable facility, produce tricationic products in high-energy impacts in which any resident 'chemical' (potential) energy is heavily augmented by kinetic energy, there are, to our knowledge, no previous examples that show the ejection of an electron from a combination of dicationic and neutral reactants in a translationally 'cold' encounter. Therefore, the subject of our SIFT study [1] is perhaps noteworthy as an indication of the reaction possibilities accessible through 'chemical' energy alone.

This caveat aside, the charge-augmentation reactions in March's comments are certainly of interest and relevance in the generic context of reactions involving multiple electron transfer, but we maintain that they do not satisfy all of the criteria required for 'double electron-transfer ionization' (DETI). Significantly, the reactions described in March's letter are all of the form of reaction (2):

$$A^+ + B \rightarrow A^- + B^{2+} \quad (2)$$

with some examples featuring autodetachment from A^- as in reaction (3):

$$A^+ + B \rightarrow A^- + B^{2+} \rightarrow A + B^{2+} + e \quad (3)$$

While the latter examples in March's letter do indeed encompass double electron transfer followed by electron liberation, they differ crucially from the Ar^{2+} + C_{60} reaction in the site of electron release. The detachment of an electron from the product (intermediate) anion is fundamentally different to the loss of an additional electron from the product cation. Reaction type (3) is, in essence, one possible outcome of 'single electron transfer ionization' (we hesitate to advance an acronym for this class of reactions!) for which we have already encountered (thermal-energy collision) examples in our own laboratory, viz. the reactions of He^+ with $C_{10}H_8$ [3] and with C_{60} [4].

So far as we can establish, March's examples all fall into the categories of 'double electron-transfer' and 'double electron-transfer with electron detachment', but do not exhibit double electron-transfer ionization. The defining characteristic for DETI, reaction (4), is that one reactant must increase its electron count by two, while the

$$A^{n+} + B^{m+} \rightarrow A^{(n-2)+} + B^{(m+3)+} + e \quad (4)$$

other loses three electrons. n = 2 and m = 0 in the example which we have presented [1].

We are very grateful to March for detailing some of the historical experimental background regarding charge-augmentation reactions. Nevertheless, we stand by our as-

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sertion [1] that reaction (5) appears to be the first example of (gas phase) double

$$Ar^{2+}(^1S_0) + C_{60} \rightarrow Ar + C_{60}{}^{3+} + e \quad (5)$$

electron-transfer ionization occurring under thermalized collision conditions.

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