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COMMENT

Reply to the 'Comment on "Treating highly charged carbon and fullerene clusters as dielectric particles"' by H. Zettergren and H. Cederquist, *Phys. Chem. Chem. Phys.*, 2012, 14, DOI: 10.1039/c2cp42883k

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In their Comment, Zettergren and Cederquist[1] raise concerns regarding a publication by Stace and Bichoutskaia[2] where single fullerene molecules were treated as dielectric particles. Zettergren and Cederquist question three separate aspects of the work: (1) the form of the equation that has been used to calculate interaction energies between charged particles; (2) whether fullerenes are better treated as metallic rather than dielectric particles, and (3) whether over-the-barrier models provide a good estimate of kinetic energy release in reaction products. Each of these points will be addressed in turn below.

An analytical solution,[3] which we recently developed for treating electrostatic interactions between charged particles of dielectric materials, includes static dielectric constants (zero frequency relative permittivity) for both the interacting particles and the medium in which the interaction occurs. The formalism[3] is clearly best suited for studying soft matter, including liquids, colloids, polymers, foams, gels, granular materials and a number of biological materials. As an example, the dielectric model[3] gives excellent quantitative agreement with experimental measurements for the electrostatic force between pairs of poly-methyl methacrylate particles in non-polar solvents.[4] However, we are also intrigued to see that the dielectric model[3] can produce reliable quantitative results for molecular interactions. Unlike the image charge method, it captures and describes correctly the induced surface charge distribution as a function of distance between particles, which leads to polarisation of interacting charged particles and provides evidence of the physical effects of the electrostatic interaction between them.[5]

The expression derived for the electrostatic force acting between two charged dielectric polarisable particles[3] is entirely consistent, and, in the limiting case of the interaction of a polarisable sphere and a point charge, agrees with the solution obtained from the theory of static and dynamic electricity.[6] The interpretation of electrostatic potential energy is, however, not so straightforward, and care must be taken to obtain the energy in a form which shows clearly the factors that are kept constant and the factors that vary with the separation between the particles (charges). In our approach[3] the electrostatic force can be related to the electrostatic interaction energy through differentiation with respect to the separation distance, *keeping the multipole moments constant* (constant charge). If a linear response of the media is assumed, the energy term describing the interaction between a permanent charge and a polarised surface charge distribution should be multiplied by a factor of 1/2. In the case of particles with low dielectric constants, however, the difference is not significant, but this discrepancy will become more important for the case of conducting interacting particles.

From our calculations we proposed that fullerenes could be reliably treated as dielectric particles;[2] in contrast, Zettergren and Cederquist[1] claim that, at least for C_{60}, the fullerene is better described as being metallic. This is a very interesting question because icosahedral C_{60} is known from experiment to have a very large HOMO–LUMO gap of 1.57 ± 0.03 eV.[7] Since it is impossible to incorporate a fullerene into an electric circuit directly, other characteristics need to be used to verify whether it behaves like a conductor or dielectric. The static and dynamic polarizabilities of C_{60} have been calculated using experimental data on the photoabsorption cross-section.[8] It has been shown[8] that C_{60} in a static electric field behaves as a collection of individual carbon atoms rather than as a conducting sphere, and its static polarizability significantly exceeds that of a conducting sphere. However, the theoretical results of Fowler and Pisanski[9] indicate that the large gap seen in C_{60} is perhaps unusual amongst fullerenes in general, and they find, for example, that C_{20} represents the other extreme of having a zero HOMO–LUMO gap. In addition, DFT calculations by Huang *et al.*[10] show that the calculated image potential for C_{60} closely resembles that of an isolated metallic sphere. Clearly, these very different conclusions from both theory and experiment are more than can be accounted for with a single parameter (dielectric constant) model.

The final part of the Comment by Zettergren and Cederquist[1] is concerned with energy partitioning following the fragmentation of both charged clusters of fullerenes and individual fullerenes fragmenting *via* the loss of either C_2^+ or C_4^+. How the energy associated with a Coulomb barrier (or any reverse activation

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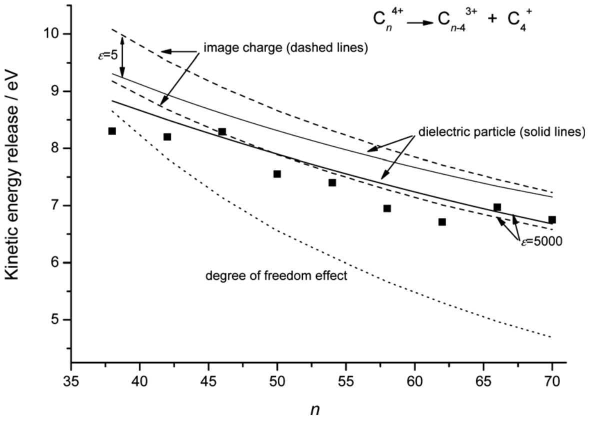

Fig. 1 Comparison between experimental kinetic energy release data[14] for reaction (1), shown as squares, and new results calculated from both the dielectric particle model (solid line) and the point charge–image charge model (dashed line) for two values of the dielectric constant (ε). Also shown as a dotted line is an estimate of how the kinetic energy might depend if partitioning of excess energy were influenced by the size of the product energy sink.

energy) is distributed following a unimolecular reaction depends critically on the shape of the potential energy surface and the structure at the barrier maximum,[11] *i.e.* either reactant-like or product-like. For examples where the separation of the reaction products can be treated as two particles, the presence of a well-defined maximum in the reaction coordinate would identify the associated structures as being product-like. That being the case, then a significant fraction of any exothermicity can be expected to appear as kinetic energy release. Recent experiments undertaken on a high resolution mass spectrometer[12,13] have provided accurate measurements of the kinetic energy release associated with charge separation in dication molecular clusters, and for at least five different molecular systems the application of a dielectric particle model gives very good agreement with the experimental results.[12,13]

With regard to the fullerene results, we have repeated, in part, the calculations that appeared in Fig. 6 of our original paper.[2] This time we have introduced a factor of 1/2 into the polarisation term of both the point charge-image charge and particle–particle equations. Fig. 1 presents the results for these new calculations for the reaction:

$$C_n^{\,4+} \rightarrow C_{n-4}^{\,3+} + C_4^{\,+} \qquad (1)$$

The results are compared with the experimental data of Senn *et al.*[14] and the image charge model. As anticipated,[1] the inclusion of the 1/2 factor reduces the contribution the attractive term makes to the height of the energy barrier, and the predicted energy releases are increased by several meV. Also included in Fig. 1 is an estimate of how the kinetic energy releases might vary according to fullerene size (n) if the size of the energy sink ($3n - 6$ vibrational degrees of freedom) had an influence on energy partitioning – clearly, that is not the case.

The theory points to the fact that polarisation of the smaller $C_4^{\,+}$ particle has a strong influence on the height of the barrier when n is small. However, what might also be concluded from these calculations is that either ε is ~ 5 and, as suggested,[1] some of the Coulomb barrier is being partitioned to the internal degrees of freedom of the fragments, or the dielectric constant is greater than 5 and there is no energy partitioning. All of which suggests the need for improvement in both the quality of the experimental data and the accuracy of the theory as applied to individual fullerenes.

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