

# A model for the charge transfer probability in helium nanodroplets following electron impact ionization

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**Abstract**

A theoretical model has been developed to describe the probability of charge transfer from helium cations to dopant molecules inside helium nanodroplets following electron impact ionization. The location of the initial charge site inside helium nanodroplets subject to electron impact has been investigated and is found to play an important role in understanding the ionization of dopants inside helium droplets. The model is consistent with a charge migration process in small helium droplets that is strongly directed by intermolecular forces originating from the dopant, whereas for large droplets (tens of thousands of helium atoms and larger) the charge migration increasingly takes on the character of a random walk. This suggests a clear droplet size limit for the use of electron impact mass spectrometry for detecting molecules in helium droplets.

## 1. Introduction

Helium nanodroplets provide a means of studying molecules and molecular clusters inside superfluid liquid helium. Electron impact mass spectrometry is one of the main means of identifying the presence of a molecule or cluster inside a helium nanodroplet and so it is important to understand the mechanism for ion formation in this environment. The basic mechanism for ion formation in doped helium droplets was initially described by Scheidemann *et al.* [1] and builds upon the ionization mechanism proposed for heavier rare gas clusters [2]. The process starts with an electron striking a helium atom somewhere in the helium droplet, causing the formation of a  $\text{He}^+$  ion. A resonant charge hopping process then takes place in which the positive charge jumps to an adjacent helium atom or, if nearby, to the dopant species. This hopping process is terminated either by the formation of  $\text{He}_2^+$  (which acts as a nucleation centre for forming larger  $\text{He}_n^+$  cluster ions), or by the irreversible formation of the dopant cation. For molecules in small helium droplets the energy release on ion formation leads to the complete evaporation of the surrounding helium atoms, leaving the bare ion in the gas phase.

The first detailed experiments designed to explore the charge hopping process in helium nanodroplets were carried out by Janda and co-workers. This work used mass spectrometry to determine the product ion yield as a function of dopant partial pressure and helium droplet size and focused on NO [2] and rare gases [4]-[6] as the dopants. By constructing a simple model of their experimental data, based on the variation of the charge transfer probability as a function of droplet size, Janda and co-workers were able to deduce that as few as 3-4 charge hops would lead to charge localization (self-trapping) on the helium, *i.e.* formation of  $\text{He}_2^+$  [4]. Consequently, according to this interpretation of the experimental data, the dopant molecule would need to be close to the site of initial ionization in order for there to be a significant probability of charge transfer.

Recent work by Lewis *et al.* has added substantially to the understanding of charge transfer processes in helium nanodroplets. In one study, the threshold photoelectron-photoion coincidence (TPEPICO) technique was employed to investigate the fragmentation mechanism and energetics of helium droplets doped with triphenylmethanol after electron impact ionization [7]. In another recent study, Lewis and co-workers developed the technique of optically-selected mass

spectrometry (OSMS) [8]. This ingenious approach combines conventional mass spectrometry with tunable laser excitation of dopant molecules to select the mass spectrometric signal from a specific type of molecule or molecular cluster in the helium nanodroplets. This is a major step forward since it makes it possible, for example, to distinguish droplets doped with a single dopant molecule from those droplets containing more than one dopant molecule or with none. This technique was used to determine the charge transfer probability for small molecules such as HCN, HCCH and HCCCN as a function of mean droplet size [8]. In support of the experimental findings, a Monte Carlo simulation of the charge transfer data was performed. The model developed was quite sophisticated and included the effect of electrostatic forces emanating from the dopant molecule on the direction of charge hopping. The variable parameter in these simulations was the number of charge hops before self-trapping, and the best agreement with experiment was obtained assuming 9 hops.

In order to fully understand the ion chemistry in helium droplets, it would be useful to have a detailed theoretical model of the charge formation and migration process in helium nanodroplets. In this work a classical model has been developed in order to interpret experimental measurements of the charge transfer probability (CTP) in doped helium droplets following electron impact ionization. In contrast to previous theoretical models, the initial charge location following electron impact is explicitly taken into account leading to a non-uniform charge distribution within the droplet. The model also takes into account the likely distribution of nanodroplet sizes, rather than treating all droplets as if they have the mean droplet size. Furthermore, the competition between charge hopping and self-trapping is described by a fixed branching ratio, rather than a fixed number of hops, which leads to the concept of a mean free path for positive charge hopping in helium droplets. The resulting model has been used to simulate some of the mass spectral data of small molecules in helium nanodroplets obtained by Lewis and co-workers using the OSMS technique. As will be shown, the agreement between experiment and simulation is good and this leads to a number of important conclusions about charge hopping in doped helium droplets.

## **2. Theoretical model**

### *A. Background*

If a molecule is present in a helium droplet composed of several thousand helium atoms, the chance of direct electron impact ionization of the molecule is very small. Consequently, electron impact ionization almost always results initially in the formation of  $\text{He}^+$  ions, which must then transfer their charge to dopant molecules by some migration mechanism.

It is generally accepted that the charge migration inside helium droplets proceeds by resonant charge hopping, a process first suggested by Atkins to account for charge migration in bulk liquid helium [9]. Charge hopping can be brought to a close by the formation of  $\text{He}_2^+$  in its  $^2\Sigma_u^+$  electronic ground state. However, at the relatively large He-He distances found in liquid helium, the separation in energy between the  $^2\Sigma_u^+$  state and the repulsive  $^2\Sigma_g^+$  state, both of which correlate to the same  $\text{He}^+ + \text{He}$  dissociation limit, is very small. Consequently, charge hopping can continue providing the distance between the helium atoms remains sufficiently large. Atkins suggested that charge localization (self-trapping to form  $\text{He}_2^+$ ) would occur as soon as the velocity of hopping excitation slowed to the local velocity of sound. Using this criterion, Scheidemann *et al.* estimated the hopping number to be in excess of  $10^3$  [1]. Recently, information derived from experimental charge transfer measurements on doped helium nanodroplets has resulted in a sharp downward revision of the hopping number. A combination of experimental data and associated models by the groups of Janda [2,3] and Miller [8] now suggests that the number of charge hops before self-trapping is  $<10$ .

Two distinct ways of treating the charge hopping process have been used in modelling experimental charge transfer data. One approach assumes that the hopping between helium atoms has unit probability below some threshold number of hops and zero beyond that (self-trapping occurs). This step-function treatment of the hopping probability was employed by Lewis *et al.* in their modelling of their OSMS data [8]. Rather than employing this step function, we choose to treat the charge hopping as a stochastic process, *i.e.*, the branching ratio between charge hopping and self-trapping is assumed to be constant at each step. Callicot and co-workers have previously employed the same assumption in modelling the charge migration in helium droplets doped with heavier rare gases [4]. The stochastic assumption is mathematically convenient and should provide a reasonable description of the mean charge hopping length. Underlying this assumption is that the charge hopping is

extremely fast such that the nuclear positions remain essentially fixed even after several hops. At the average He-He distances in liquid helium of 3.16 Å [1] the  $\text{He}_2^+$  system is almost at its dissociation limit. A quantum mechanical estimate by Halberstadt and Janda found that at this distance each charge hop takes around 20 fs [10]. We have performed a CCSD(T)/6-311++G(d,p) calculation of the  $^2\Sigma_u^+$  potential energy curve of  $\text{He}_2^+$ , from which the force between two helium atoms can be derived. According to this calculation the He-He<sup>+</sup> distance will be altered by no more than 0.003 Å in 20 fs assuming two static helium atoms separated initially by 3.16 Å. It is therefore reasonable to assume that the charge will hop through an essentially fixed nuclear framework where the self-trapping probability per hop is independent of time.

By ascribing a fixed self-trapping probability to each hop, the competition between self-trapping and resonant charge hopping during the charge migration process can be expressed as  $dQ = -(Q/\Gamma_{He}) dl$ , where  $Q$  is the total charge inside a helium droplet beam in the form of  $\text{He}^+$ ,  $l$  is the distance traveled by the positive hole, and  $\Gamma_{He}$  is the free mean path of the positive hole inside helium droplets. Over time, self-trapping means that the proportion of charge that remains in the form of  $\text{He}^+$  declines exponentially with the distance traveled according to:

$$Q(l) = Q_0 \exp(-l/\Gamma_{He}) \quad (1)$$

Here  $Q_0$  is the total charge before migration begins (and thus  $l = 0$ ). Note that the decline of charge in the form of  $\text{He}^+$  means that there will be a concomitant decline in the charge transfer probability to any dopant in a helium nanodroplet, since self-trapping eliminates this possibility. This exponential decay of charge transfer probability is the starting point of the model developed here.

### *B. Initial charge location inside helium droplets*

To evaluate the probability of charge transfer from the helium to the dopant molecule, it is necessary to know where the positive charge is initially created. In the models developed by the groups of Janda [4] and Miller [8], the probability for finding the initial charge on a specific helium atom was assumed to be uniform across the droplet.

This may be justifiable for small droplets, but it is almost certainly a poor approximation for large droplets. We have therefore attempted to account for any variation in the charge distribution throughout the helium droplet.

To determine the charge distribution, the cross sections for electron-helium atom collisions determined by Fursa and Bray have been employed [11]. For an electron colliding at an energy of 40 eV, which is the energy used in obtaining the experimental data with which we compare our results later, the total collision cross section  $\sigma_t$  is  $2.06 \times 10^{-16} \text{ cm}^2$ , while the ionization cross section is  $1.7 \times 10^{-17} \text{ cm}^2$ . The mean free mean path of the electron,  $\Gamma_e$ , can be calculated as  $1/n\sigma_t$ , where  $n$  is the number density of helium atoms inside helium droplets calculated from the bulk liquid helium density of  $125 \text{ kg m}^{-3}$  [12]. This gives  $\Gamma_e = 25.9 \text{ \AA}$  for an electron having 40 eV of energy. Assuming a spherical droplet containing  $N$  helium atoms, the radius of the droplet for  $^4\text{He}$  is given by  $R = 2.22 N^{1/3}$  [13]. Consequently, taking as an example a helium droplet containing 3,000 helium atoms, the radius is  $32 \text{ \AA}$  and the probability that the incident electron will reach the center free of collision is calculated to be 29% if it is heading initially in the correct direction.

For the sake of simplicity, the path followed by the incoming electron is assumed to be a straight line through the helium. For small droplets this is a reasonable approximation given that the number of He- $e^-$  collisions is expected to be low. Even for rather large droplets with a radius of  $100 \text{ \AA}$  (91,400 helium atoms) the average He- $e^-$  collision number is only five. The result of these collisions will be a tendency to create more ions near the surface of the cluster.

Consider a positive charge that is created by the incident electron at  $(r, \theta, \phi)$  in a polar coordinate system with the origin at the centre of a helium droplet of radius  $R$ . The  $z$  axis is defined as pointing along the direction of travel of the electron. From basic geometry, the distance the electron must travel to reach this point in a straight line path is  $\sqrt{R^2 - r^2 \sin^2 \theta} - r \cos \theta$ . Consequently, the electron penetration probability at a distance  $r$  from the droplet centre can be described as:

$$f(r) = 2\pi r^2 \int_0^\pi \exp\left\{-\left(\sqrt{R^2 - r^2 \sin^2 \theta} - r \cos \theta\right)/\Gamma_e\right\} \sin \theta d\theta \quad (2)$$

where  $\Gamma_e$  is the mean free path of the electron defined above.

Neglecting inelastic scattering, the ionization probability at each location is directly proportional to the penetration probability. To see the effect on the charge distribution, we show the findings for droplets with radii of  $100 \text{ \AA}$  (91,400 helium atoms) and  $R = 30 \text{ \AA}$  (containing 2,500 helium atoms) in Figure 1. It is evident that even for the smaller helium droplets there is a significant decrease in ionization probability in moving from the surface towards the centre. In practice the lower density of helium expected in the surface and near-surface layers [14], which is not accounted for here but which is discussed again later, may partially counteract this fall-off. Consequently, the assumption of a uniform charge distribution for droplets with a few hundred or a few thousand helium atoms is probably a reasonable approximation. However, for larger droplets there will remain a strong radial dependence, which means that the initial positive charge is unlikely to be found anywhere near the centre of the helium droplet.

### C. The total charge created in a helium droplet beam

The charge contained within the droplet beam is a function of the size distribution of the helium droplets. To take this into account, we make the standard assumption of a log-normal distribution for the droplet sizes, *i.e.*

$$P(N, \sigma) = \frac{1}{\sqrt{2\pi N\sigma}} e^{-\frac{(\ln(N)-\mu)^2}{2\sigma^2}} \quad (3)$$

where  $P$  is the probability that a droplet contains  $N$  helium atoms,  $\mu$  is the mean value of  $\ln(N)$  and  $\sigma$  is the standard deviation of the normal distribution. The log-normal distribution has been shown to be valid for helium nanodroplets by Lewerenz *et al.*, who used a scattering method for determining the sizes of liquid helium droplets [15]. Three sets of cluster size distributions at different temperatures were measured by Lewerenz *et al.*, and from the maximum and mean values of each distribution we have employed the expressions  $N_{\max} = \exp(\mu - \sigma^2)$  and  $\langle N \rangle = \exp(\mu + \sigma^2 / 2)$  to estimate the standard deviation as  $\sigma = 0.65$ . This value of  $\sigma$  is assumed in the expressions given below.

In terms of the droplet radius, the probability distribution in (3) can be converted to

$$P(R, \sigma) = \frac{3}{\sqrt{2\pi R \sigma}} e^{-\frac{\left(3 \ln\left(\frac{R}{\rho}\right) + \frac{\sigma^2}{2}\right)^2}{2\sigma^2}} \quad (4)$$

where  $\rho$  is the droplet radius at the mean droplet size, *i.e.*  $\rho = 2.22 \langle N \rangle^{1/3}$

Taking into account both the distribution of nanodroplet sizes and the distribution of initial locations of the positive charge following electron impact, the total charge  $Q$  created in a helium nanodroplet beam with a mean droplet size  $\langle N \rangle$  can be expressed as

$$Q(\rho) = C_1 \int_0^\infty \frac{1}{R \sigma} e^{-\frac{\left(3 \ln\left(\frac{R}{\rho}\right) + \frac{\sigma^2}{2}\right)^2}{2\sigma^2}} \int_0^R \int_0^\pi \exp\left\{-\left(\sqrt{R^2 - r^2 \sin^2 \theta} - r \cos \theta\right) / \Gamma_e\right\} r^2 \sin \theta \, d\theta \, dr \, dR \quad (5)$$

Here  $C_1$  is a coefficient whose magnitude is proportional to the flux of the helium droplets.

#### *D. The charge transfer probability*

There are two extreme views of the charge transfer process. One assumes that charge transfer from helium atom to helium atom is essentially a random walk consisting of a fixed number of hops. If the charge reaches the dopant before the maximum number of hops is attained then charge transfer can occur. At the other extreme we could assume that, with a dopant placed inside the droplet, long-range charge-induced dipole interactions will steer the charge hopping such that it follows a direct path from the initial site of ionization towards the dopant. We shall, without justification at this stage, assume the latter. Furthermore, it will also be assumed that the dopant is fixed at the centre of the helium droplet. The credibility of these issues will be discussed later.

From the discussion in section 2A, an exponential decline in the probability for transferring charge to the dopant as a function of distance between the positive charge and the dopant is expected if we assume a straight-line journey of the charge from initial location to dopant. Equation (1) can thus be modified to obtain

$$g(r) = C_2 \exp(-r/\Gamma_{He}) \quad (6)$$

In the above expression  $g(r)$  represents the charge transfer probability and the constant  $C_2$  reflects the probability of charge transfer from  $\text{He}^+$  to the dopant when the charge reaches a helium atom in contact with the dopant.

Combining equations (2), (4) and (6), the total charge transferred to the dopant becomes

$$Q_D(\rho) = C_1 \int_0^\infty \frac{1}{R\sigma} e^{-\frac{\left(3\ln\left(\frac{R}{\rho}\right) + \frac{\sigma^2}{2}\right)^2}{2\sigma^2}} \int_0^R \int_0^\pi \exp\left\{-\left(\sqrt{R^2 - r^2 \sin^2 \theta} - r \cos \theta\right)/\Gamma_e\right\} r^2 \exp\{-r/\Gamma_{He}\} \sin \theta \, d\theta \, dr \, dR \quad (7)$$

The charge transfer possibility,  $CTP(\rho)$ , is then given by

$$CTP(\rho) = \frac{Q_D(\rho)}{Q(\rho)} \quad (8)$$

where  $Q(\rho)$  and  $Q_D(\rho)$  are given by equations (5) and (7), respectively.

### 3. Simulation procedure

The expressions described above have been used to simulate the experimental findings for HCCCN and HCN obtained using OSMS by Lewis *et al.* [8]. Analytical formulae cannot be derived for the integrals in equations (5) and (7) and so these have been evaluated numerically. The *NIntegrate* routine in Mathematica was used to carry out these multidimensional integrations.

A non-linear fitting program based on the Marquardt least-squares fitting algorithm was written in Mathematica<sup>®</sup> 5.2 to perform the simulation. The upper integration limit for the helium droplet size in the integrals was set at  $20R$ , which means that the largest helium droplets included in the integral evaluation were some 8,000 times larger than the average helium droplet size under consideration, which more than covers all possibilities. This was confirmed by increasing the upper integration limit further in trial calculations, which was found to have no significant

impact on the outcome of the simulation. Only two parameters have to be fitted in the program,  $C_2$  and  $\Gamma_{He}$ , since  $C_1$  disappears through cancellation in equation (8).

#### 4. Results

Figure 2 presents the simulations for HCN and HCCCN based on the model described above. It can be seen that in both cases the agreement between simulation and experiment is good. Lewis and co-workers also obtained OSMS data for HCCH [8], which in principle could also be simulated in the present work. Unfortunately, fewer experimental data points were recorded for HCCH and in particular the absence of any data points for droplets with <1800 helium atoms, a region where the charge transfer probability declines rather quickly, will make any fit seem inaccurate. Consequently, the HCCH data have not been simulated in this work.

For HCCCN we obtain  $C_2 = 1.15 \pm 0.04$  and  $\Gamma_{He} = 35.2 \pm 1.9 \text{ \AA}$ , while for HCN the result is  $C_2 = 0.92 \pm 0.05$  and  $\Gamma_{He} = 32.2 \pm 2.7 \text{ \AA}$ . The dopant is treated as a featureless point object in the present model, and thus in this limit the mean free paths should be the same in both cases. Within the margin of error of the simulation, this is indeed found to be the case. Halberstadt and Janda calculated that the mean hopping distance between adjacent helium atoms is close to  $3.1 \text{ \AA}$  [10]. If this is combined with the mean free path determined in our simulations, then it implies that the positive hole hops from one helium atom to another approximately 11 times before the charge becomes self-trapped. Of course in our model there is no maximum hop number, only an exponentially decaying probability.

The constant  $C_2$  reflects the probability that charge will transfer to the dopant when it reaches an adjacent helium atom. A value of unity implies that charge transfer is inevitable. Consequently, the values of 1.15 and 0.92 for HCCCN and HCN obtained from the fit come close to the expectation of a high charge transfer probability. Within the context of the simple ‘hard sphere’ type of model described here, it makes no sense for  $C_2$  to be larger than unity, which it clearly is for HCCCN. However, given that our model takes no account of the size, structure and charge distribution within a dopant molecule, it would be unwise to attach too much importance to the value of  $C_2$ . The larger value of  $C_2$  when compared with HCN may simply reflect the larger size of the HCCCN molecule, which could allow the positive

hole to transfer over to the dopant at distances further from the droplet centre than is possible for HCN.

As described earlier, Janda and co-workers have used standard electron impact mass spectrometry to determine charge transfer probabilities for rare gas and NO dopants in helium nanodroplets [2-5]. We have also performed simulations of these results. This is illustrated by the case of NO [3], for which we derived  $\Gamma_{He} = 7.7 \pm 0.6$  Å and  $C_2 = 4.6 \pm 0.6$ . In contrast to the OSMS data for HCN and HCCCN, the  $C_2$  constant is unfeasibly large. We take this to indicate that the charge transfer probabilities determined for NO and the rare gases by Janda and co-workers are less reliable than those determined from OSMS data. The statistical nature of the pick-up process inevitably means that there will be some droplets with no dopant molecules while others will have more than one, which complicates the interpretation of charge transfer probabilities derived from standard (non-OSMS) electron impact mass spectrometry.

## 5. Discussion

### *A. Random walk versus directed charge hopping*

A key assumption in this work is that the dopant resides at the centre of the droplet and draws the positive hole towards itself in a straight-line path. Even in the absence of the dopant the positive charge will be drawn towards the centre of the droplet, since this is the location where solvation by the surrounding helium is at its maximum [16]. However, while there are two factors in play to direct the charge hopping motion, it is not clear that these are sufficient to enforce an approximately straight line path. In this context it is interesting to note that Lewis and co-workers [8] attempted to analyze their OSMS data by carrying out Monte Carlo simulations of the charge hopping process. Included in these simulations were explicit potential gradients for the ion-dopant interaction derived from *ab initio* calculations. The direction of charge hopping was weighted by a Boltzmann-like factor to take into account more favorable and less favorable hopping directions. However, it was found that a Boltzmann weighting yielded indistinguishable results from a comparable simulation in which the charge travelled directly along the potential gradient towards the dopant [8]. This

would seem to suggest that the ion-molecule interactions are strong enough to drive the positive charge directly toward the dopant molecule.

To test this assumption further, the charge transfer probabilities in this work have also been calculated assuming a random walk. The random walk means that, on a sphere of radius of  $r$ , the positive charge has an equal possibility of reaching any part of the spherical surface. Consequently, the probability that the positive charge reaches the dopant is proportional to  $1/4\pi r^2$ . Thus the effect of a random walk model is achieved simply by removing the  $r^2$  term from equation (8).

Two tests have been performed with the  $r^2$  term removed: one without the term  $\exp(-r/\Gamma_{\text{He}})$  (equivalent to a self-trapping mean free path of  $\Gamma_{\text{He}} = +\infty$ ) and the other with  $\Gamma_{\text{He}} = 33.65 \text{ \AA}$ . The effect this has on the simulations is shown in Figure 3 for HCCCN alongside the results from the directed hopping mechanism. Note that the curves (b) and (c), which correspond to  $\Gamma_{\text{He}} = +\infty$  and  $\Gamma_{\text{He}} = 33.65 \text{ \AA}$ , respectively, have been rescaled by a factor of 50 and have not been fitted to the data. The reason why no fit was attempted will become clear from inspection of the plot. No matter what the value of  $\Gamma_{\text{He}}$ , the random walk model leads to a rapid decay in the charge transfer probability as the average size of the droplets grows, which is inconsistent with the much slower decay observed experimentally. We take this finding as strong evidence that the positive hole migration from helium atom to helium atom is strongly biased towards the dopant molecule, *i.e.* the random walk model is not applicable, at least for droplets with only a few thousand helium atoms.

### *B. Uniform versus non-uniform initial charge distributions*

In previous simulations of charge transfer in helium nanodroplets it has been assumed that electron impact has an equal probability of creating a positive charge on any helium atom in the nanodroplet. This assumption is expected to become less reliable as the droplet size increases, as was illustrated by the data shown in Figure 1. If the uniform charge distribution is invalid, then simulations based on this assumption will overestimate the initial charge distribution near the centre of the helium droplet. This effect is probably unimportant for very small droplet sizes when calculating the probability of charge transfer to the dopant in small helium droplets but it will become an important factor for very large helium droplets. Furthermore, because of the log-

normal distribution of helium droplet sizes, even for beams with a small mean droplet size there will still be some much larger droplets within the beam under consideration.

The net effect of any model that imposes a uniform charge distribution will be to underestimate the number of charge hops. This may in part account for the slightly smaller hopping numbers found in the work of Lewis *et al.* [8] and Janda and co-workers [4], although of course there are also other differences between our model and theirs. A test run of the fitting programme assuming a uniform charge distribution has been carried out in order to compare the results with the non-uniform charge distribution. This can be easily achieved by setting  $\Gamma_e = +\infty$ . This calculation gives  $C_2 = 1.18 \pm 0.04$  and  $\Gamma_{\text{He}} = 32.9 \pm 1.9 \text{ \AA}$  for HCCCN and  $C_2 = 0.94 \pm 0.05$  and  $\Gamma_{\text{He}} = 30.4 \pm 2.7 \text{ \AA}$  for HCN, which indicates that  $\sim 10$  hops are required for  $\text{He}^+$  to become self-trapped. The smaller hopping number obtained from these simulations is consistent with the hopping number derived by Lewis and co-workers from their own simulations [8].

If we accept a hopping time of  $\sim 20$  ps [10], 11 hops corresponds to 220 ps. Although the phenomenological model employed in the current study does not explicitly consider the mechanism by which  $\text{He}_2^+$  forms, we note that the timescale for self-trapping calculated in the present work is not inconsistent with models for  $\text{He}_2^+$  formation. For example, Scifoni *et al.* have employed quantum mechanical calculations to determine the 3-body relaxation time to form  $\text{He}_2^+$  following direct electron impact ionization of a helium atom in a helium trimer at the number density of liquid helium [17]. The total relaxation time was estimated to be on the order of 1 ps, with initial quenching to the highest vibrational states of  $\text{He}_2^+$  taking several hundred fs. As soon as  $\text{He}_2^+$  begins to form the charge hopping process is irreversibly terminated. In view of the approximations involved in the calculations performed by Scifoni *et al.* and in the present phenomenological model, the agreement between timescales is quite good.

### *C. Charge transfer in large helium droplets*

In the limit of very large helium droplets the probability of charge transfer to the dopant, assuming it is located somewhere near the centre of the droplet, will become vanishingly small. In their investigation of triphenylmethanol in helium droplets,

Miller and co-workers claimed that this point was reached when the helium droplets achieved an average size of approximately 40,000 helium atoms, as evidenced by the very small dopant signal in the mass spectrum [7]. This concurs roughly with our own experimental findings, although in our laboratory we have managed to obtain mass spectra with droplets with an estimated mean size of up to 60,000 atoms [18].

Any conclusion about the charge transfer behavior for large droplet sizes based on the present study is difficult to make with confidence because the simulations presented here are derived from comparison with experimental data for mean droplet sizes of  $<10,000$  helium atoms. Nevertheless, we cautiously note that extrapolation of the simulated curves gives a very slow fall-off in charge transfer probability such that, even for a droplet with 50,000 helium atoms, the probability remains as high as 12% for HCN and 17% for HCCCN. Consequently, something else must be happening to curtail the charge transfer process.

As the droplet size increases, the probability distribution for the site of initial ionization by electron impact becomes increasingly skewed towards distances further from the droplet center. At large distances the potential gradient generated by the dopant will be weaker and therefore less effective at steering the direction of charge hopping. In effect what will happen is a gradual switch from directed charge hopping to a random walk as the droplet size increases. As discussed earlier, this results in a much more rapid decay in the charge transfer probability with helium nanodroplet size, which could account for the difference between the experimental findings and the extrapolation of the simulated data.

Of course there are other factors that might also be significant. For example, in large helium droplets the energy released on charge transfer to the dopant might not be sufficient to evaporate away all the helium atoms. In such circumstances it would not be possible to observe the dopant ion in the mass spectrum because of the large number of attached helium atoms, even though charge transfer may still have occurred. Thus at this stage, without additional experimental data on the charge transfer probability for droplet sizes  $>10,000$  helium atoms, we cannot be sure of the reason why the charge transfer probability declines so rapidly for larger droplets,

#### *D. Limitations of the current model*

Lehmann has described an effective Hamiltonian for the motion of neutral impurities inside helium droplets [19] which includes both long-range electrostatic interaction

between the dopant and atomic helium, and hydrodynamic contributions. It was found that the effective potential for motion of the dopant is determined by the long-range part of the dopant-helium interaction, which contains both isotropic and anisotropic terms. The isotropic term will confine the impurity near the centre of the clusters, while the weaker anisotropic term couples the translational motion with the rotation of the dopant molecule and can drive the molecule off centre. For a helium droplet of 3 nm radius (consisting of 2,500 helium atoms) and containing a HCN molecule, the location of maximum probability was found to be 1.2 nm from the centre of the droplet. Of course this distribution is spherically symmetric and so the mean position of the dopant for a large collection of doped droplets would be at the centre of a droplet.

In principle it is possible to take the distribution of dopant positions into account in our calculations. Assuming the site where the charge first appears is located at  $(r_1, \theta_1, \phi_1)$  and the dopant is at position  $(r_2, \theta_2, \phi_2)$ , the distance between the charge and the dopant  $d$  can be calculated using basic trigonometry as:

$$d = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_1 \cos \theta_2 \cos(\phi_1 - \phi_2) - 2r_1r_2 \sin \theta_1 \sin \theta_2} \quad (9)$$

We denote the distribution function along the radial direction as  $P(R, r_2)$ , and thus the charge transferred to the dopants can be derived by modifying equation (7) to obtain:

$$Q_D(\rho) = C_1 \int_0^\infty \frac{1}{R\sigma} e^{-\frac{\left(3\ln\left(\frac{R}{\rho}\right) + \frac{\sigma^2}{2}\right)^2}{2\sigma^2}} \int_0^R \int_0^\pi \int_0^{2\pi} \exp\left\{-\left(\sqrt{R^2 - r_1^2 \sin^2 \theta} - r_1 \cos \theta_1\right) / \Gamma_e\right\} \\ r_1^2 \sin \theta_1 \left\{ \int_0^R \int_0^\pi \int_0^{2\pi} P(R, r_2) r_2^2 \exp\{-d / \Gamma_{He}\} \sin \theta_2 d\phi_2 d\theta_2 dr_2 \right\} d\phi_1 d\theta_1 dr_1 dR \quad (10)$$

Lehmann [19] derived the distribution function (equivalent to  $P(R, r_2)$  in equation (10) ) for a neutral species inside liquid helium droplets using a quantum mechanical model. The larger the droplet the flatter the confining potential energy well over the central region of the droplet, with the result that the dopant distribution function becomes broader as the droplet size increases. However, because this distribution is isotropic the average effect over a large collection of nanodroplets will be equivalent to a dopant located at the centre of the droplet. Consequently, it should be acceptable

in the current model to ignore the substantial variation in dopant positions inside a helium droplet. Lewis and co-workers reached a similar conclusion in their simulation of their OSMS data, finding that simulations that included the off-centre dopant distribution did not differ significantly from those carried out with the dopant fixed at the centre of the droplet [8].

Another simplification we have employed is to assume that the density of the helium throughout the droplets is the same as that of bulk liquid helium. However, in practice it is known that there is a sheath of low-density helium near the surface where the density falls from 90% of its bulk value down to 10% over a distance in the region of 6 Å [15]. We have not attempted to explicitly allow for this effect, which will tend to underestimate the degree of electron penetration into the droplet. However, its effect will only be significant for the smallest droplets considered in the present work. Furthermore, we note that its impact will partly be offset by the neglect of electron scattering by the helium, which has the consequence of overestimating the degree of electron penetration. Although these two approximations will not cancel fully, the residual effect is not expected to be large.

## 6. Conclusions

A classical model based on a constant branching ratio between positive hole hopping and charge self-trapping (to irreversibly form  $\text{He}_2^+$ ) in helium nanodroplets has been described. This has been used to simulate charge transfer probabilities in doped helium nanodroplets measured by optically selected mass spectrometry. The fit between theory and experiment is good and makes it possible to draw a number of conclusions. First, we calculate a mean free path of 34 Å for the charge hopping in helium, which corresponds to approximately 11 hops before charge self-trapping occurs. This is similar to the hopping numbers deduced by other research groups using different models.

It has been shown for droplets containing  $< 10^4$  helium atoms that the charge transfer probabilities are inconsistent with charge migration by a random walk. Instead the direction of charge migration is strongly biased in a direction pointing directly towards the dopant species. However, an extrapolation of our model to droplet sizes in excess of  $10^4$  helium atoms suggests a slower decay with  $\langle N \rangle$  than observed experimentally. As the droplet size increases, the initial positive charge is more likely to be produced in a region far from the droplet centre, and thus the

interaction between the charge and the dopant molecule will be weaker. In the limit of a large separation the guiding force experienced by the positive hole due to the dopant will be negligible and the charge hopping will instead show the characteristics of a random walk. The lack of measured charge transfer probabilities for droplets with  $> 10^4$  helium atoms makes it difficult to assess when the switchover from directed hopping to a random walk occurs. However, a combination of the experimental observations and simulations suggests that this crossover occurs at between  $10^4$  and  $5 \times 10^4$  helium atoms. This switch to random walk behavior means that for droplets with  $\gg 5 \times 10^5$  helium atoms the probability of charge transfer to a dopant molecule becomes negligibly small.

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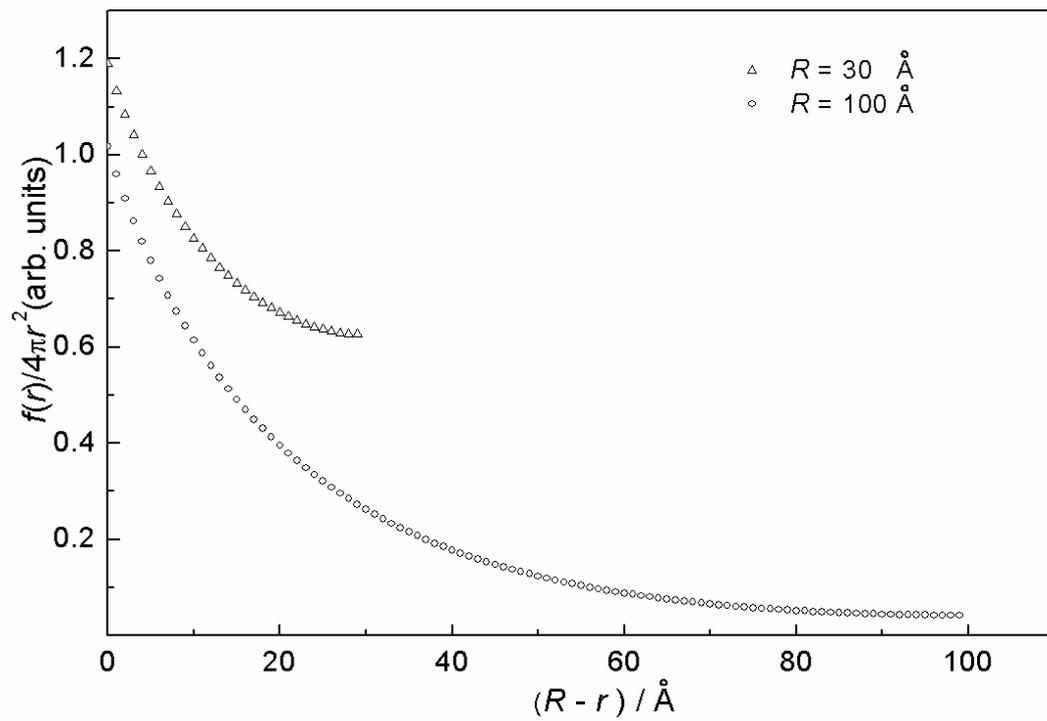


Figure 1 Variation of the electron radial penetration probability as a function of the distance,  $r$ , from the centre of the helium droplet. The calculation was carried out assuming an electron impact energy of 40 eV.

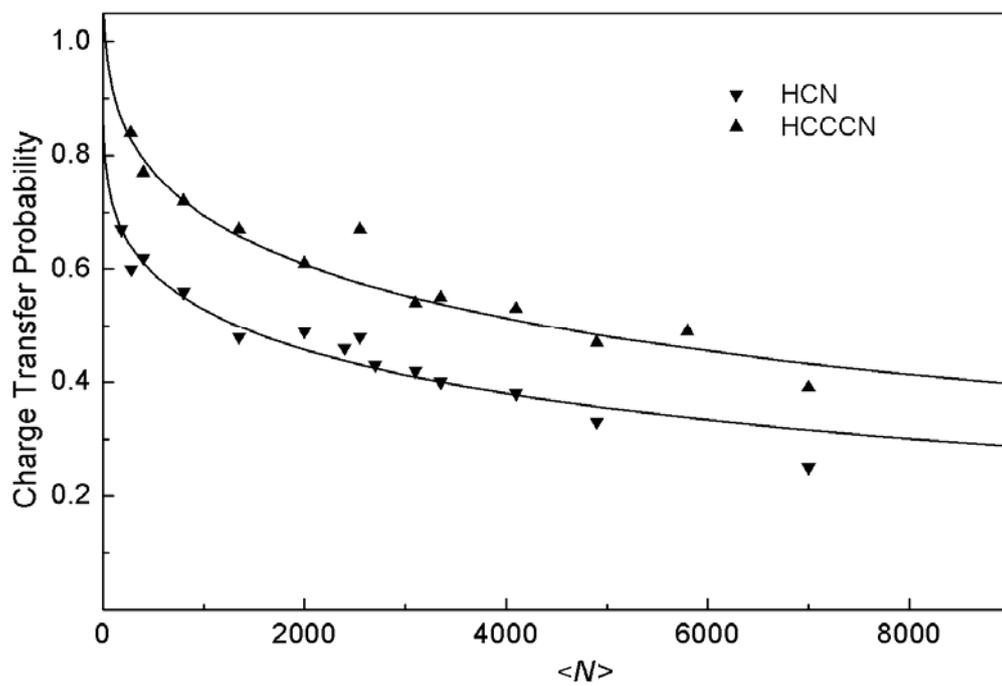


Figure 2 Comparison of the simulated charge transfer probability with the experimental values for HCN and HCCCN [10]. The solid lines represent the simulation while the individual points have been extracted from experiment.

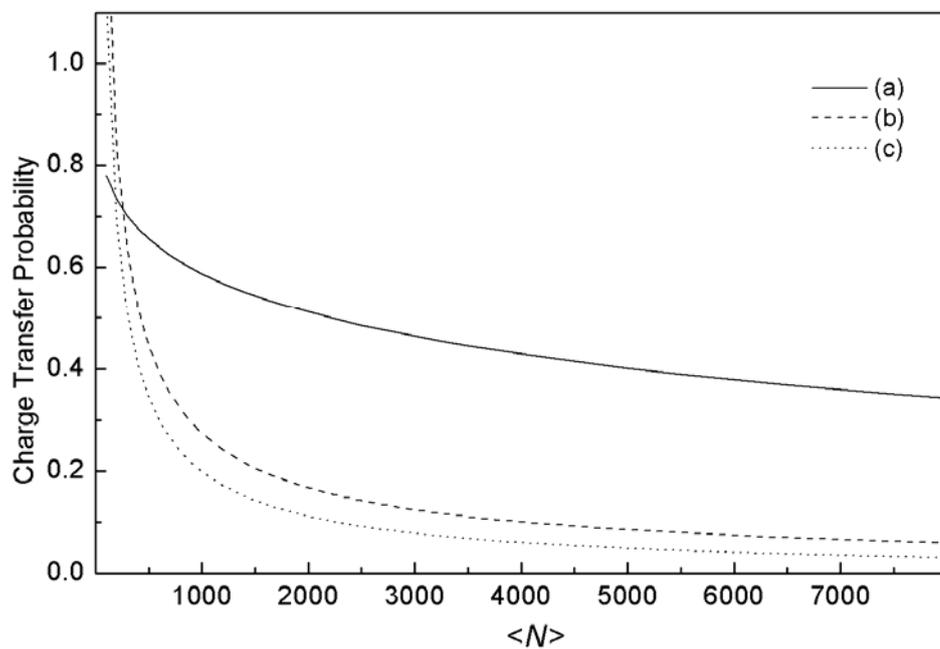


Figure 3 (a) Comparison of the simulation obtained for HCCN with random hopping models derived for (b)  $\Gamma_{\text{He}} = +\infty$  and (c)  $\Gamma_{\text{He}} = 33.7 \text{ \AA}$ .