

# Charge transfer within He clusters

Berton E. Callicoatt, David D. Mar, V. A. Apkarian, and Kenneth C. Janda  
*Department of Chemistry and Institute of Surface and Interface Science, University of California, Irvine,  
California 92697*

(Received 31 July 1996; accepted 27 August 1996)

Mass spectrometric measurements of clusters containing  $N$  helium atoms and an NO molecule yield probabilities for charge transfer from  $\text{He}^+$  to NO that range from  $0.8 \pm 0.1$  for  $\langle N \rangle = 540$  to  $0.02 \pm 0.02$  for  $\langle N \rangle = 15\,000$ . From this we estimate that the  $\text{He}^+$  hole hops approximately 70 times before localization at a  $\text{He}_2^+$  core. © 1996 American Institute of Physics.  
[S0021-9606(96)03341-7]

Recently, several research groups have begun to study the properties of liquid He clusters as a “solvent” for atoms and molecules.<sup>1–12</sup> There are several important motivations for this work. Since He clusters remain liquidlike down to their steady state temperature of 0.4 K,<sup>4</sup> they provide a unique environment for studying chemical processes. Although helium clusters provide the least perturbative condensed phase environment in the chemical sense, the low temperature and rapid relaxation dynamics, or high thermal conductivity, of liquid He will have profound effects on the types of processes that can be observed. For instance, it has recently been shown that weakly bonded states of alkali dimers and trimers can be stabilized on the surface of a He cluster for spectroscopic investigation.<sup>8</sup> It has also been shown that  $\text{SF}_6$  molecules inside liquid He clusters can be studied by high resolution infrared spectroscopy<sup>4,6,7</sup> and that the spectra reveal surprising rotational dynamics within the cluster.<sup>4</sup> The environment in a large helium cluster also has profound effects on fragmentation patterns upon ionization. For instance, ionization of  $\text{SF}_6$  in a helium cluster results in considerable intensity at the parent ion peak, which is completely absent for ionization of  $\text{SF}_6$  in the gas phase.<sup>2</sup> In a series of seminal papers,<sup>1–5,13,14</sup> Toennies and co-workers have examined the scattering of atoms and molecules from liquid He clusters and the mass spectrometry of liquid He clusters containing one or more “dopant” atoms or molecules. Among the many interesting results presented in these papers is clear evidence that the sequential “pick-up” technique can be used to “coagulate” small subclusters of arbitrary composition within the liquid He cluster.<sup>3</sup>

Studies of helium clusters will have the problem common to most cluster studies that no specific cluster composition can be isolated from the cluster distribution. To fully take advantage of this enticing low temperature phenomenon, it would be very helpful to develop reliable techniques for the analysis of cluster composition. As might be expected, electron impact ionization of He clusters leads to extensive fragmentation. For clusters that contain  $10^3$ – $10^4$  He atoms, the most intense mass peak observed is  $\text{He}_2^+$ . Mass peaks of higher oligomers fall gradually in intensity with peaks up to about  $\text{He}_{50}^+$  having significantly intensity. However, Toennies and colleagues have found that if the He cluster contains a dopant atom or molecule, the parent ion of the dopant usually becomes the most intense peak in the

mass spectrum.<sup>3</sup> The conclusions of Toennies *et al.* can be summarized by a set of “rules” for the ionization process. (1) The first step in the ionization process can be best characterized as ionization of an individual He atom, probably near the surface of the cluster. (2) On time scales of  $\approx 10^{-12}$  s the hole created by the initial ionization event diffuses throughout the cluster by resonant hole migration until it localizes, either on the dopant molecule, or by self-trapping on a  $\text{He}_2^+$  core.<sup>2</sup> (3) The energy released by the charge localization process serves to evaporate most or all of the He atoms. (4) If more than one dopant molecule is deposited into the cluster, the attractive forces between the two dopant molecules causes them to coagulate on a time scale of  $\approx 10^{-9}$  s, and usually the subcluster that is formed will survive ionization. If these rules apply to most clusters that are studied, then mass spectrometry would prove to be far more useful for characterizing He clusters than it has been for other types of clusters because the fragmentation patterns would be easy to understand.

In this communication we report mass spectrometric studies of NO doped large He clusters. The data yields the probability of charge transfer from a  $\text{He}^+$  ion to the NO dopant molecule versus the probability of charge localization on a  $\text{He}_2^+$  moiety. The charge transfer probability is  $0.8 \pm 0.1$  for clusters with  $\langle N \rangle = 540$  He atoms and one NO molecule, and drops to  $0.02 \pm 0.02$  for clusters with  $\langle N \rangle = 15\,000$  He atoms. ( $\langle N \rangle$  is the mean number of He atoms for the cluster distribution.) We also measure the charge transfer probability for clusters that contain two or more NO molecules, and find that the values are somewhat larger than for clusters that contain a single NO molecule. Finally, we measure the probability that  $(\text{NO})_2$  species fragment upon ionization by charge transfer and find that fragmentation is small for the  $\langle N \rangle = 15\,000$  clusters, but high for the smaller clusters.

The apparatus on which these experiments are performed employs a He cluster source similar to that developed by the group of Scoles.<sup>6–8</sup> Our pick-up region is about 10 cm long placed behind the skimmer, and we use a quadrupole mass spectrometer employing an ionization electron energy of 65 eV. The size of the He clusters was varied by controlling the temperature of the nozzle while maintaining a constant backing pressure of 20 bar. This allows us to use previously published data to estimate the cluster size

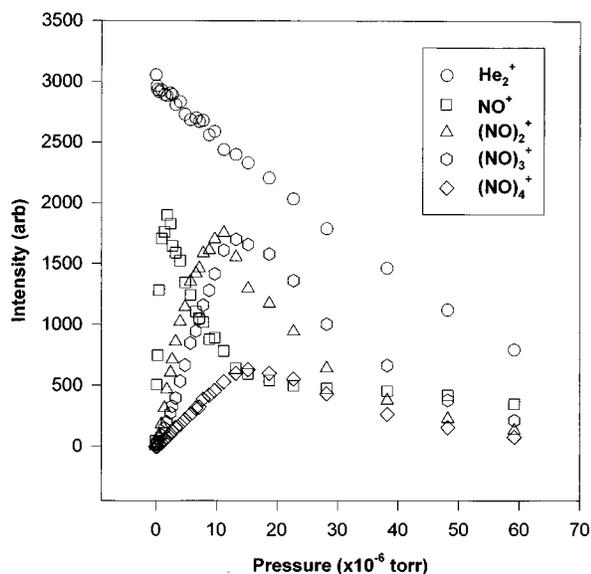


FIG. 1. The intensities of  $m/e = 8, 30, 60, 90,$  and  $120$  amu, which are due to  $\text{He}_2^+$ ,  $\text{NO}^+$ ,  $(\text{NO})_2^+$ ,  $(\text{NO})_3^+$ , and  $(\text{NO})_4^+$ , respectively, versus NO pressure in the pick-up region for beam conditions that yield a mean initial cluster size of 15 000 He atoms ( $T_0 = 11.0$  K,  $P_0 = 20$  bar). That the initial (positive) slope of the  $\text{NO}^+$  pressure dependence is much larger than the initial (negative) slope of the  $\text{He}_2^+$  pressure dependence indicates that charge transfer from  $\text{He}^+$  to NO is inefficient. Simulations of the data give a value for the charge transfer probability of  $0.02 \pm 0.02$ .

distribution for a given nozzle temperature.<sup>14</sup> The NO pressure in the pick-up region is controlled with a leak valve and measured with an ionization gauge. Figure 1 shows the intensity of several  $m/e$  peaks as a function of the NO pressure in the pick-up region for He clusters with  $\langle N \rangle = 15000$  atoms. The  $\text{He}_2^+$  ion intensity,  $m/e = 8$ , is representative of the flux of large He clusters that ionize without charge transfer to NO. The  $\text{NO}^+$ ,  $(\text{NO})_2^+$ ,  $(\text{NO})_3^+$ , and  $(\text{NO})_4^+$  ions are detected by monitoring peaks at  $m/e = 30, 60, 90,$  and  $120$ , and their intensities reveal the extent of both charge transfer and fragmentation of the cluster.

As expected, the  $\text{NO}^+$  intensity grows rapidly with increasing NO pressure in the pick-up cell (see Fig. 1). The  $\text{NO}^+$  intensity reaches a maximum and starts to decrease for NO pressures above  $3 \times 10^{-6}$  Torr due to the fact that clusters are picking up multiple NO molecules. Above this pressure, all clusters contain at least one NO molecule and the typical cluster contains not only one, but several NO molecules, yet the  $\text{He}_2^+$  intensity has only slightly decreased. This is an unambiguous indication that the probability of charge transfer from  $\text{He}^+$  to NO is small. If the hole could migrate throughout the cluster prior to self trapping then the charge would always transfer to the dopant and no  $\text{He}_2^+$  mass peak would be observed. Figure 2 shows similar data but for clusters with  $\langle N \rangle = 5500$  He atoms. In this case the  $\text{He}_2^+$  intensity decreases more quickly relative to the increase in the  $\text{NO}^+$  intensity. This shows that the probability of charge transfer from  $\text{He}^+$  to NO is larger for the smaller clusters. Also, notice that the peak intensities for the  $(\text{NO})_2^+$  and  $(\text{NO})_3^+$  ions are much less than that of  $\text{NO}^+$  for the  $\langle N \rangle = 5500$  clusters (Fig. 2), whereas the peak intensities

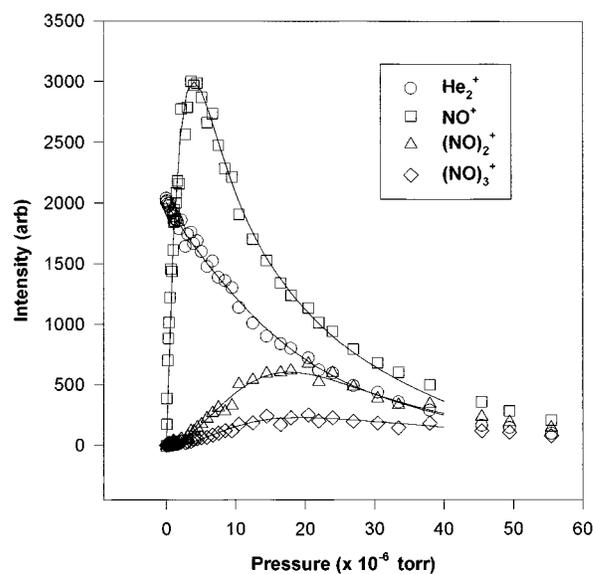


FIG. 2. Data similar to that of Fig. 1, but for an initial cluster distribution with mean size of 5500 He atoms ( $T_0 = 14.7$  K,  $P_0 = 20$  bar). In this case the magnitude of the slope for the  $\text{He}_2^+$  peak is considerably larger than in Fig. 1, even though the smaller clusters will have fewer collisions with NO at a given NO pressure. This indicates that charge transfer probability from  $\text{He}^+$  to NO for these clusters is considerably higher than for the larger clusters of Fig. 1. Simulations are consistent with a charge transfer probability of  $0.15 \pm 0.05$ . The lines through the data points are the results of such a simulation. Note also, the relative intensity of  $(\text{NO})_2^+$  compared to  $\text{NO}^+$  is much smaller for these clusters than for the larger clusters of Fig. 1. This is clear evidence that significant fragmentation occurs upon charge transfer to  $(\text{NO})_2$  species.

of the three species are similar for the  $\langle N \rangle = 15000$  clusters (Fig. 1). This shows that the fragmentation patterns of the NO cluster ions are quite different for the two He cluster sizes.

In order to make more quantitative estimates for the charge transfer and fragmentation probabilities as a function of cluster size, the data were compared to simulations. The simulations consist of two parts. First, the pick-up of NO molecules as a function of NO pressure in the pick-up region is simulated. Second, the fragmentation upon ionization is simulated. The following assumptions are employed. (1) The probability that an NO molecule is picked up is proportional to  $N^{2/3}$  where  $N$  is the number of He atoms in the cluster. (2) For each NO molecule that is picked up, 160 He atoms are evaporated to dissipate the kinetic and potential energy involved in the  $\text{He}_N\text{-NO}$  interactions, and 100 He atoms are evaporated to dissipate the energy of coagulation of NO with another NO. These evaporation processes are assumed to occur very quickly on the time scale of translation of the cluster through the pick-up cell. (3) The ionization cross section of the cluster is assumed to be proportional to  $N^{2/3}$ . For each cluster size, the charge transfer probabilities,  $p_n$ , from  $\text{He}^+$  to  $(\text{NO})_n$  are employed as a set of variable parameters. (4) For each subcluster size,  $(\text{NO})_m$ , a set of coefficients was used to give the fraction of clusters that fragmented to give particular daughter ions. For each simulation, the beam is initially assumed to consist of helium clusters with the mean cluster size for the nozzle temperature used to acquire that

TABLE I. Fractional charge transfer and fragmentation vs cluster size.  $\langle N \rangle$  is the mean number of He atoms in the cluster after one NO molecule is picked up,  $p_1$  is the fractional charge transfer from  $\text{He}^+$  to NO for a cluster that contains one NO molecule,  $p_2$  is the fractional charge transfer from  $\text{He}^+$  to NO or  $(\text{NO})_2$  for clusters that contain two NO molecules.  $f$  is the probability that  $(\text{NO})_2$  fragments upon ionization. The numbers in parentheses correspond to the uncertainty in the least significant digits.

Source temp. (K)	$\langle N \rangle$	$p_1$	$p_2$	$f$
11.0	15 000	0.02(2)	0.03(2)	<0.1
14.7	5300	0.15(5)	0.28(5)	0.85
16.5	1840	0.38(7)	0.48(7)	$\approx 1.0$
18.0	540	0.8(1)	0.9(1)	$\approx 1.0$

set of data. The ability of the simulations to reproduce the observed data is shown in Fig. 2. The fits are equally good for the other three nozzle temperatures for which simulations were performed.

Table I lists the values obtained for the fractional charge transfer as a function of the He cluster size for four mean cluster sizes. (We use the mean cluster size for clusters after a single NO molecule has been picked up.) The values drop from  $p_1 = 0.8 \pm 0.1$  for  $\langle N \rangle = 540$  to  $p_1 = 0.02 \pm 0.02$  for  $\langle N \rangle = 15\,000$ . The error bars are obtained by visually judging what range of parameters give a sufficiently good fit to the data. The estimate for the mean cluster size is obtained by comparing our source conditions to those of Lewerenz *et al.*,<sup>14</sup> who measured the cluster size distribution as a function of source conditions, and subtracting 160 He atoms to compensate for the energy that must be dissipated when an NO molecule is trapped. Table I also gives an estimate for  $p_2$ , the fraction of charge transfer from  $\text{He}^+$  to NO when the cluster contains two NO molecules. The  $p_2$  values are mainly determined by the shape of the  $\text{He}_2^+$  intensity curve as a function of the NO pressure in the pick-up cell. The pressure dependence of the  $(\text{NO})_2^+$  peak is more sensitive to the fragmentation parameters.

It is very interesting how quickly the probability of charge transfer from  $\text{He}^+$  to NO drops with increasing mean He cluster size. The drop in the charge transfer probabilities with cluster size would be even faster for size selected clusters beams. In Fig. 3 we plot estimates for the initial size distributions for each of our four nozzle temperatures based on the results of Toennies and co-workers.<sup>14</sup> Even though the present measurements only involve four different size distributions, and therefore do not allow for a deconvolution of the charge transfer probability versus cluster size, it is still tempting to speculate on what the function might be. Although there is a significant literature for charge migration in condensed rare gas media<sup>15</sup> there is still considerable room for speculation regarding the special case of He clusters.

Given the rapid drop in the charge transfer probability with increasing cluster size, we test a model in which charge transfer probability is unity for clusters with  $N_0$  or fewer He atoms, and the charge transfer probability is  $N_0/N$  for larger clusters. We then solve for  $N_0$  for each of the four cluster distributions and obtain values of  $400 \pm 100$ ,  $500 \pm 100$ ,  $550 \pm 150$ , and  $200 \pm 200$  for  $\langle N \rangle = 540$ , 1840, 5300, and

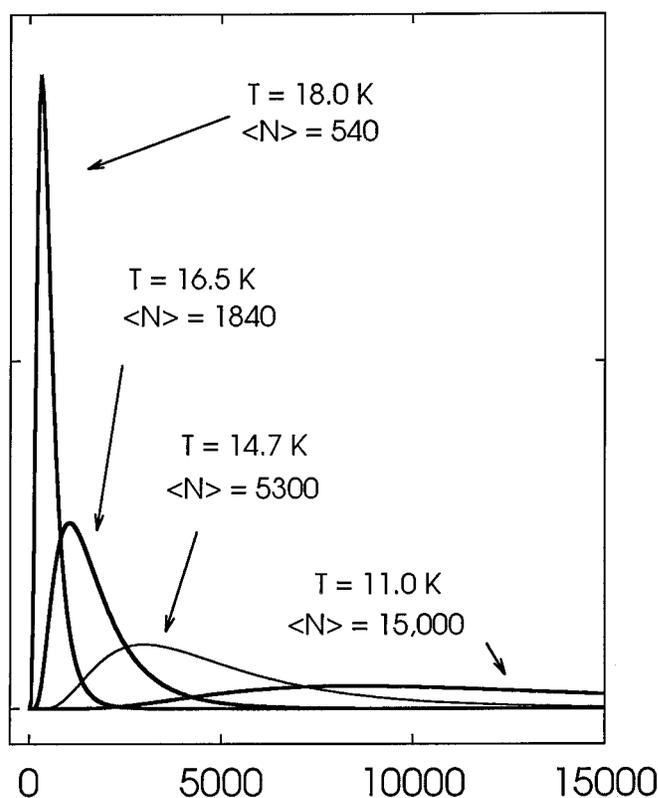


FIG. 3. Estimated size distributions for the three source temperatures employed in this study,  $T_0 = 11.0, 14.7, 16.6,$  and  $18.0$  K.

15 000, respectively. Except for the largest clusters, the value obtained for  $N_0$  is roughly constant, giving this model some credibility. The simplest interpretation is that the migrating hole travels a characteristic distance prior to self-trapping, and if the path passes within a nearest neighbor of the NO molecule, the charge is transferred. (Here we assume that the NO molecules are randomly distributed within the cluster.<sup>12,14</sup>) We expect that charge transfer is only possible to NO molecules that are nearest neighbors to a  $\text{He}^+$ , and therefore we assume a cross section of seven helium atoms for the cylindrical volume swept out by the migrating charge. An  $N_0$  value of 500 then roughly corresponds to a cylinder length of 70 hops before localization to  $\text{He}_2^+$ . This is far fewer hops than estimated by Toennies.<sup>2</sup> For the smaller clusters we would expect that the typical site is visited more often than for larger clusters, and this is consistent with the fact that the calculated  $N_0$  value increases slightly in going from  $\langle N \rangle = 540$  to  $\langle N \rangle = 5300$ . However, the small  $N_0$  value obtained for the  $\langle N \rangle = 15\,000$  clusters is difficult to explain with this model.

Another conclusion that can be drawn from the data is that the charge transfer probability  $p_2$  is larger than  $p_1$ . That is the charge transfer from  $\text{He}^+$  to NO is more likely to occur if there are two NO molecules in the cluster rather than one. (Although the error bars for these two numbers overlap, they are correlated in such a way that the error for the difference is less than the sum of the two error bars.) This trend continues as the number of NO molecules in the cluster increases. In the next paragraph we conclude that multiple NO

molecules inside a cluster completely coagulate, so this increase in charge transfer probability shows that the distance over which charge transfer occurs is at least slightly larger for  $(\text{NO})_2$  as an acceptor than for NO as an acceptor.

The fragmentation probabilities for  $(\text{NO})_2$  upon ionization for the four cluster sizes are also reported in Table I and show an interesting dependence on cluster size. For the largest clusters studied,  $\langle N \rangle = 15\,000$ , the fragmentation probability is less than 10%, but for the three smaller cluster sizes the fragmentation probability is over 80%. In fact, the  $(\text{NO})_2^+$  ion was not even observed for the two smallest cluster sizes. The simulations are consistent with two different interpretations. Either the numbers given above reflect the fragmentation probability, as stated, or they reflect the probability that the NO molecules never coagulate in the first place. However, since the second interpretation would require that NO molecules coagulate in large clusters, but not in small clusters, we conclude that the data is indeed measuring the fragmentation probability. The data also show that the main fragmentation daughter for  $(\text{NO})_2$  is not a "clean"  $\text{NO}^+$  ion but rather a distribution of  $\text{NOHe}_n^+$  ( $n = 1-15$ ) ions. In fact, the probability of producing  $\text{NOHe}_n^+$  daughter ions is significantly higher for clusters that initially contain two NO molecules than for clusters that contain only one NO molecule. Apparently, enough energy is used to break the NO-NO bond so that less energy is available to evaporate the He.

This is the first attempt to measure the efficiency of charge transfer within He clusters, so clearly there is much more to be learned. Among the interesting issues are questions concerning the charge migration rate and directionality. For instance, are the rates different near the surface of the cluster compared to the bulk of the cluster? Is there a barrier for the charge to go from the surface to the center of the cluster? It may also be possible to determine whether the distribution of dopant molecules is random. In this preliminary report, we have shown, and performed simulations for, a small fraction of the total available data. More complete

simulations of a larger fraction of the available data will be very time consuming because of the number of parameters that must be included. Also, the next stage of simulations should include the distribution of cluster sizes in the beam. Our experience with this initial study makes us optimistic that extensions of this type of work will determine the charge transfer and fragmentation mechanisms in He clusters in considerable detail.

This research was made possible through an AFOSR Grant No. F49620-1-0251, under the University Research Initiative. Also, we acknowledge the support of the University of California, Irvine, Academic Senate Committee on Research, and the National Science Foundation, for funds used to purchase the mass spectrometer used in this study.

- <sup>1</sup>A. Scheidemann, B. Schilling, J. P. Toennies, and J. A. Northby, *Physica B* **165**, 135 (1990).
- <sup>2</sup>A. Scheidemann, B. Schilling, and J. P. Toennies, *J. Phys. Chem.* **97**, 2128 (1993).
- <sup>3</sup>M. Lewerenz, B. Schilling, and J. P. Toennies, *J. Chem. Phys.* **102**, 8191 (1995).
- <sup>4</sup>M. Hartmann, R. E. Miller, J. P. Toennies, and A. Vilesov, *Phys. Rev. Lett.* **75**, 1566 (1995).
- <sup>5</sup>M. Hartmann, R. E. Miller, J. P. Toennies, and A. Vilesov, *Science* **272**, 1631 (1996).
- <sup>6</sup>S. Goyal, D. L. Schutt, and G. Scoles, *Phys. Rev. Lett.* **69**, 933 (1992).
- <sup>7</sup>S. Goyal, D. L. Schutt, and G. Scoles, *J. Phys. Chem.* **97**, 2128 (1993).
- <sup>8</sup>F. Stienkemeier, J. Higgins, W. E. Ernst, and G. Scoles, *Phys. Rev. Lett.* **74**, 3592 (1995).
- <sup>9</sup>R. N. Barnett and K. B. Whaley, *J. Chem. Phys.* **99**, 9730 (1993).
- <sup>10</sup>R. N. Barnett and K. B. Whaley, *Z. Phys. D* **31**, 75 (1994).
- <sup>11</sup>Y. K. Kwon, D. M. Ceperley, and K. B. Whaley, *J. Chem. Phys.* **104**, 2341 (1996).
- <sup>12</sup>E. Krotscheck and S. A. Chin, *Chem. Phys. Lett.* **227**, 143 (1994).
- <sup>13</sup>H. Buchenau, E. L. Knuth, J. Northby, J. P. Toennies, and C. Winkler, *J. Chem. Phys.* **92**, 6875 (1996).
- <sup>14</sup>M. Lewerenz, B. Schilling, and J. P. Toennies, *Chem. Phys. Lett.* **206**, 381 (1993).
- <sup>15</sup>See, for instance, N. Schwentner, E.-E. Koch, and J. Jorner, *Electronic Excitations in Condensed Rare Gases* (Springer-Verlag, Berlin, 1985).
- <sup>16</sup>M. A. McMahon, R. N. Barnett, and K. B. Whaley, *J. Chem. Phys.* **104**, 5080 (1996).