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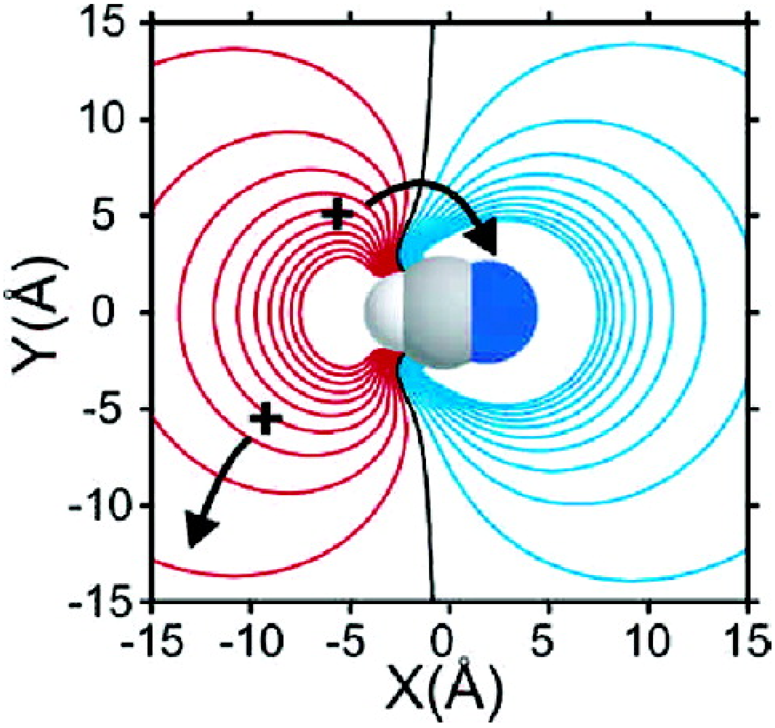

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Probing Charge-Transfer Processes in Helium Nanodroplets by Optically Selected Mass Spectrometry (OSMS): Charge Steering by Long-Range Interactions

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Abstract: Electron impact ionization of a helium atom in a helium nanodroplet is followed by rapid charge migration, which can ultimately result in the localization of the charge on an atomic or molecular solute. This process is studied here for the cases of hydrogen cyanide, acetylene, and cyanoacetylene in helium, using a new experimental method we call optically selected mass spectrometry (OSMS). The method combines infrared laser spectroscopy with mass spectrometry to separate the contributions to the overall droplet beam mass spectrum from the various species present under a given set of conditions. This is done by vibrationally exciting a specific species that exists in a subset of the droplets (for example, the droplets containing a single HCN molecule). The resulting helium evaporation leads to a concomitant reduction in the ionization cross sections for these droplets. This method is used to study the charge migration in helium and reveals that the probability of charge transfer to a solvated molecule does not approach unity for small droplets and depends on the identity of the solvated molecule. The experimental results are explained quantitatively by considering the effect of the electrostatic potential (between the charge and the embedded molecule) on the trajectory of the migrating charge.

Introduction

Helium nanodroplets have received considerable attention in recent years, as outlined in a recent review,[1] because of their nearly ideal spectroscopic characteristics regarding molecular and cluster solutes.[2−5] Unfortunately, the analogous experiments in bulk helium have not been forthcoming, given that helium is such a poor solvent that molecules tend to condense quickly onto any container walls that might exist.[6] In contrast, unsupported helium nanodroplets are better solvents than the surrounding vacuum, meaning that in such systems the solute molecules of interest are generally located somewhere in the interior of the droplets.[7,8] There are a few exceptions to this rule, however, most notably alkali metal atoms and clusters, which are expelled to the surface of the droplets.[9]

Electron impact ionization mass spectrometry is often used as a detection method in pure and doped helium nanodroplet studies,[8,10,11] making the associated ionization processes also of considerable interest and the subject of several previous studies.[12−16] In infrared laser spectroscopic studies in helium nanodroplets, mass spectrometric detection is based upon the fact that each vibrational excitation of solvated molecules results in the evaporation of several hundred helium atoms, thus reducing the sizes of the droplets, which in turn decreases their ionization cross sections. It is now well-known that electron impact ionization mass spectra of doped helium nanodroplets show peaks that are due to pure helium ion clusters, He_n^+, as well as the ionized solute and its fragments.[13−16] Numerous studies have revealed that the embedded molecules are ionized through a charge migration mechanism first discussed by Atkins.[17] The process begins with the electron impact ionization of a helium atom in the droplet. Indeed, this is by far the most likely initial event, given that direct ionization of a solvated

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† Analytical R & D.

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molecule is relatively improbable in a droplet containing several thousand helium atoms. Further support for this mechanism comes from studies of droplets doped with SF_6[12] and argon clusters[15] which show that the electron energy threshold for the signals in the mass spectrum is consistent with the ionization energy of He^+, namely, 24.6 eV, and is independent of the identity of the embedded dopant.

Once the He^+ ion is formed within the droplet, resonant charge transfer between adjacent helium atoms[13] allows the charge to rapidly (on the time scale of femtoseconds[18]) migrate through the droplet. The ultimate result of this charge "hopping" is either the transfer of the charge to the molecular dopant or the formation of a He_n^+ ($n \geq 2$) cluster ion.[19] In the former case, the large difference in the ionization energies of helium and the molecule (about 10−15 eV) results in the liberation of sufficient energy to evaporate the droplet, resulting in substantial cooling of the newly formed molecular ion. As a result, this ionization channel leads to the formation of the bare molecular ion and its fragments. In fact, the cooling results in substantially more parent ion than typically observed in a gas-phase electron impact ionization mass spectrum.[20] Alternatively, the formation of the He_n^+ ion also releases enough energy to desolvate the He_n^+ ion,[19] so that subsequent charge transfer to the dopant molecule is unlikely. Interestingly, for much larger droplets on the order of 10^5−10^6 atoms, a qualitatively different behavior is observed in which the charges remain solvated.[21] For smaller droplets (those with fewer than 10 000 atoms), desolvated ions are observed,[19] and the competition between charge transfer to the dopant and formation of a He_n^+ ion has been studied by Janda and co-workers as a function of droplet size. They concluded from studies of droplets doped with neon,[14] argon,[15] and xenon[16] clusters that the charge undergoes resonant transfer between adjacent helium atoms (referred to as a hop) approximately three times before the formation and desolvation of a He_n^+ ion. As expected for such a mechanism, the probability of charge transfer to the dopant atom or cluster decreases with increasing droplet size, simply because the average distance between the initially formed He^+ ion and the dopant increases with droplet size. In the limit of very large droplets, the charge-transfer probability to the dopant can become so small that the associated ion signals are no longer detectable.[20]

As noted above, ionization in helium nanodroplets can result in less ion fragmentation because the parent ion is evaporatively cooled by the helium.[7,12,20] In a previous study on the cooling of trimphenylmethanol (TPM) ion in helium,[20] we showed that this cooling mechanism is ultimately limited by the charge-transfer probability, given that in the largest droplets, which have the greatest potential for cooling the ion, the charge never reaches the impurity molecule. However, for droplets of medium size, the fragmentation patterns reflect the evaporative cooling of the ions. The experimental results suggested that helium cooling is most effective in large molecules, where the lifetimes of the hot molecular ions are sufficiently long[22,23] so that the helium has time to cool the system before it undergoes fragmentation. In contrast, previous studies on the fragmentation of SF_6 in helium, once again using electron impact ionization, indicate that the helium is rather ineffective in preventing fragmentation,[12] presumably owing to the very short lifetime of the SF_6^+ ion, which does not allow sufficient time for cooling.

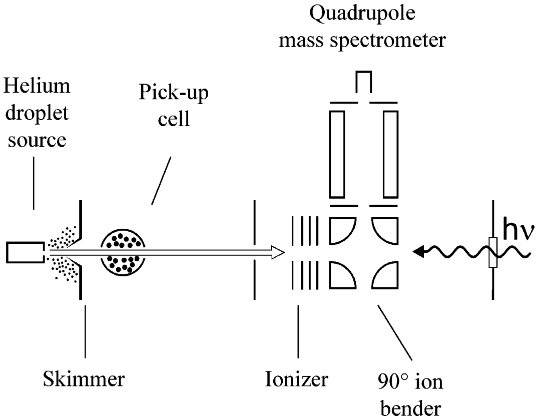

Figure 1. A schematic diagram of the apparatus used to obtain optically selected mass spectra. Droplets are formed by expanding high-pressure helium through a low-temperature nozzle. The droplets are then doped using a pickup cell before entering an electron impact ionizer. Following droplet ionization, the resulting ions are bent out of the droplet beam and into a quadrupole mass spectrometer. An infrared laser is counterpropagated along the droplet beam and is used to "tag" droplets containing the species of interest (see text).

Quantitative experimental studies of the charge-transfer processes discussed above are complicated by the fact that the helium nanodroplet beams are not monodispersed[24] and the pickup process used to dope them with molecular solutes follows Poissonian statistics.[7] Consequently, the overall mass spectrum of a droplet beam has contributions from a wide distribution of species formed within droplets of varying size. This makes it necessary to account for the relative abundances of empty droplets and those containing one or more dopant molecules, including the effects of fragmentation, to obtain quantitative information on these charge-transfer mechanisms. While studies of this type have been carried out for rare gas dopants[14−16] and simple diatomic molecules (NO),[13] it is clearly desirable to develop experimental methods that avoid these complications. In the present study, we make use of a modification of the infrared laser spectroscopy methods mentioned above to obtain mass spectra of helium nanodroplet beams with species selectivity. An amplitude modulated infrared laser is used to excite a particular solute molecule, allowing us to modulate the signals associated with only those droplets containing the species of interest. This optically selected mass spectrometry (OSMS) provides results that are more directly related to the charge-transfer process discussed above.

Experimental Section

The experimental apparatus used in the present study is shown schematically in Figure 1. The helium nanodroplet source consists of a 5-μm diameter nozzle, the temperature of which can be varied from 10 to 30 K (cooled by a closed-cycle helium refrigerator). Droplets were formed by expanding ultrahigh purity helium from approximately 90 bar. The expansion is skimmed by a 0.4-mm diameter aperture located approximately 20 mm downstream of the source. The resulting

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beam consists of a log-normal distribution of droplet sizes,[24] the mean size varying according to published scaling laws[25] from 1000 to 7000 helium atoms, depending upon the temperature of the nozzle. The droplets are doped with the molecules of interest by passing the droplet beam through a "pickup" cell containing HCN, HCCCN, or $H^{13}C^{13}CH$ (herein referred to as HCCH), at a pressure optimized for the pickup of a single molecule. These systems were chosen in light of their strong C−H vibrational absorption bands that lie within the tuning range of our lasers, which have permitted their previous spectroscopic study in helium.[26−28] A continuous wave and tunable periodically poled lithium niobate OPO (PPLN−OPO)[29] was used to vibrationally excite the solvated molecules. The excitation efficiency was optimized by having the laser counter propagate along the entire droplet beam path, resulting in an overlap region between them of approximately 60 cm.

In the present study, the helium droplets were ionized by electron impact and the resulting ions were bent 90° into a quadrupole mass spectrometer (Extrel/Merlin), located perpendicular to the droplet beam. The electron energy was set to 40 eV to avoid double ionization of the helium droplets.[20,21] Each vibrational excitation of a particular dopant molecule results in the evaporation of several hundred helium atoms. This evaporation reduces the ionization cross section of the laser excited droplets,[24] thus decreasing the probability that they will be ionized. Droplets that are empty, contaminated, or doped with a species not in resonance with the infrared laser remain unaffected. Thus, by modulating the infrared laser and using phase-sensitive detection, we are able to record a mass spectrum corresponding to only those droplets containing the species of interest, namely, the one excited by the laser. In general, the infrared spectra of helium-solvated molecules are very well resolved,[26−28] making this a powerful method for discriminating between the various species present in the droplet beam.

Since the charge-transfer probabilities determined in the present experiment depend directly on the response of the mass spectrometer to different masses, it was necessary to calibrate the sensitivity of the spectrometer over the mass range of interest. This was done by tuning the ion optics in the spectrometer so that the gas-phase mass spectrum of trifluoromethane agreed with the spectrum in the NIST database.[30] The resulting calibration was also verified with several other molecules from the database. We estimate that the relative peak intensities in the mass spectra presented here are accurate to approximately 3% over the entire mass range.

Application of OSMS to Clusters in Helium Nanodroplets

In a previous spectroscopic study,[31] we showed that HCN clusters formed in helium nanodroplets are exclusively linear, owing to the long-range dipole forces that act to orient the molecules as they approach one another. The fast cooling by the helium then prevents isomerization of the linear chain into the more stable cyclic clusters.[31] These systems provide us with an interesting demonstration of the OSMS technique, allowing us to characterize their fragmentation upon electron impact ionization of the droplets. The infrared spectrum displayed in Figure 2 corresponds to excitation of the "free" C−H stretches of these complexes, namely, $(HCN)_n$, $n = 1-5$ and beyond. This spectrum was recorded by tuning the laser, while monitoring the laser-induced decrease in the droplet size. As discussed elsewhere,[27] the rotational constant of HCN in helium is large enough so that only the $J = 0$ state is thermally populated at the droplet temperature, so that only the $R(0)$ transition is observed, near 3313.5 cm^{-1}. In contrast, the HCN dimer shows a well resolved P and R branch structure,[32] characteristic of a linear molecule, while for the longest chains (such as HCN pentamer[31]) only the P and R branch contours are resolved.

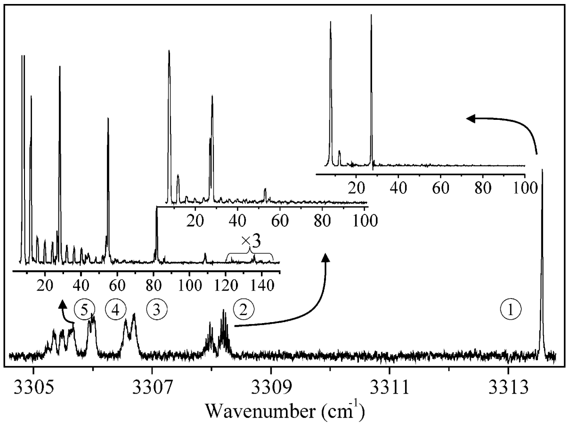

Figure 2. An infrared spectrum of HCN multimers formed in helium droplets (bottom). Vibrational bands associated with the monomer through pentamer are labeled 1−5, respectively. The optically selected mass spectra (insets) were collected with the laser tuned into resonance with the bands associated with the HCN monomer, dimer, and pentamer.

The insets in Figure 2 show OSMS spectra recorded by tuning the laser into resonance with transitions associated with the HCN monomer, dimer, and pentamer. In the OSMS spectrum of the HCN monomer (labeled 1), the He_n^+ ion peaks are evident,[19] along with one additional peak at 27 amu, corresponding to HCN^+. A normal mass spectrum of helium droplets typically shows a significant peak at 18 amu, because of the pickup of background water. No such peak is evident in the OSMS spectra, since the water-contaminated droplets have an infrared spectrum that is shifted from that of the HCN monomer. Similarly, droplets containing HCN multimers are also not excited by the laser, so that the corresponding ion signals are absent. When the laser frequency is tuned to the HCN dimer band (labeled 2), a distinctly different OSMS spectrum is observed. Once again, the He_n^+ ions are observed in the mass spectrum, along with peaks in the region of the HCN monomer (27 amu) and dimer (54 amu). Careful inspection of this spectrum reveals that the peak near the monomer ion is actually a doublet, corresponding to the formation of HCN^+ and $HCNH^+$ upon ionization of a droplet containing the dimer, indicative of two different fragmentation channels, that is, loss of a neutral HCN and protonation ($(HCN)_2^+ \rightarrow HCNH^+ + CN$), respectively. It is important to emphasize that this is not simply a "low pass filter" technique, but rather it is completely selective for only the pumped species. In particular, the 27 amu peak observed in the dimer OSMS spectrum is due entirely to fragmentation of the dimer ion and not from the fragmentation of larger clusters or from ionized HCN monomer.

The final OSMS spectrum in Figure 2 results from tuning the laser into resonance with the HCN pentamer band. In this

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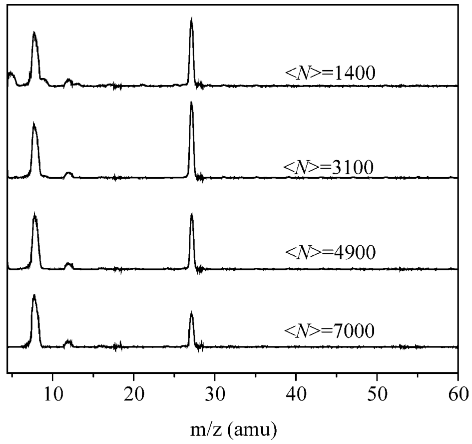

Figure 3. Optically selected mass spectra of HCN monomer in helium droplets, for several different mean droplet sizes ⟨*N*⟩. In large droplets, the $[HCN]^+$ peak ($m/z = 27$) is small, relative to the helium ions, indicating inefficient charge transfer (see text). In small droplets, charge transfer is more efficient, and He_nH^+ ions are observed because of fragmentation of the HCN^+ molecular ion.

case, $(HCN)_n^+$ ions are observed for $n = 1-5$, indicative of the fragmentation pattern for the HCN pentamer ion. Once again, close inspection of this spectrum reveals that the peaks corresponding to $(HCN)_n^+$, $n = 1-4$, are all split into doublets, corresponding to the neutral elimination and protonation channels discussed above for the dimer. The relative intensities of the fragment peaks vary with the helium droplet size, indicative of the effects of evaporative cooling on the branching ratios to the various fragmentation channels. Although a study of the details of these fragmentation patterns may be warranted in its own right, it is beyond the scope of the present study. Rather, we simply present the above data as an example of the power of OSMS in separating out the contributions to the overall helium nanodroplet mass spectrum, allowing us to focus on the species of particular interest in the charge-transfer problem.

Droplet Size Dependence of Charge Transfer

As demonstrated in the previous section, OSMS provides us with a direct measurement of the mass spectrum of a single species solvated in helium nanodroplets. However, this method still samples the entire droplet size range, as we will discuss in detail below. In this section, we focus on using OSMS to measure the charge-transfer probabilities for many simple molecules, with the goal of understanding the factors that control the migration of charge within the droplets. We begin with a more thorough investigation of the HCN monomer in helium, the OSMS spectra for which are shown in Figure 3 as a function of the mean droplet size. Since these mass spectra correspond to droplets containing precisely one HCN molecule, the relative intensities of the He_n^+ and HCN^+ peaks reflect the relative likelihoods of charge transfer to the HCN molecule ("successful" charge transfer) and the formation of He_n^+.

It is immediately evident from comparing these mass spectra that the intensity of the HCN^+ peak decreases relative to those of the He_n^+ ions with increasing droplet size, indicative of the corresponding reduction in the charge-transfer probability. This is consistent with our expectations and with previous studies of other systems.[13−16] However, OSMS provides us with a direct means to quantify the charge-transfer probabilities, because species selection has been accomplished. In practice, we simply integrate the areas under all of the peaks in the OSMS spectra, assigning each to either a helium ion channel (no charge transfer) or to molecular ionization channel (successful charge transfer). The charge-transfer probability (CTP) is then defined as the sum of the areas under the peaks associated with the molecular ionization channel divided by the total integrated area under all of the peaks. The contribution to the overall intensity from He_n^+ peaks with $n > 25$ was insignificant and was neglected in the following analysis. The He^+ peak, typically observed in the mass spectra of droplets, is absent from the OSMS spectrum (although not shown here since there is considerable noise on mass 4 amu from background helium gas). This is consistent with the fact that previous studies have shown that the signals on mass 4 amu come primarily from atomic helium that is present in the beam rather than from the ionization of droplets.[19] The relative ionization cross sections for the solvated molecule and the helium atoms do not come into play in these studies and so are not required in the analysis of the data, because in both channels it is the helium that is initially ionized by the electron impact process.

For large droplets, which provide effective cooling of the newly formed molecular ion,[20] the only peak in the mass spectrum that comes from the molecular ionization channel is HCN^+. However, for the smaller droplets (for example, droplets with a mean size of 1400), there are several new peaks that appear at odd mass numbers, in the range 5−21 amu. These peaks are absent from the ordinary mass spectrum of empty helium droplets, indicating that they arise from the molecular ionization channel. The appearance of these features is consistent with gas-phase studies, which indicate that the lowest energy fragmentation channel for HCN is $H^+ + CN$,[33,34] leading us to the conclusion that in the smaller droplets the HCN^+ undergoes fragmentation. The H^+ then goes on to cluster or react[35] with helium atoms, giving rise to the mass peaks observed in the OSMS spectrum. The intensity in these peaks must then be added to the "successful" charge-transfer channel (molecular ionization). Once again, the droplet size dependence of the molecular fragmentation is worthy of further study in its own right, but is beyond the scope of the present study.

Experiments were carried out for many more droplet sizes for the dopants hydrogen cyanide, cyanoacetylene, and acetylene and were analyzed in the manner discussed above. The charge-transfer probabilities (CTP) obtained from these measurements are summarized in Figure 4 for HCN (open squares), HCCCN (solid triangles), and HCCH (solid circles). The solid lines through the different data sets are simple quadratic fits to the data and are meant only to help guide the eye. In all three cases, the CTP decreases with increasing droplet size, indicative of the fact that it is correspondingly less likely that the charge will find the molecule. The droplet sizes shown take into account the evaporation of helium atoms (several hundred atoms[7]) because of pickup of a dopant molecule, using estimates of the thermal energy of the dopant molecules obtained from ab initio (MP2/6-311++G**) calculations.[36] As mentioned above, the mean droplet sizes (prior to pickup) are determined from scaling laws,[25] and using a procedure described previously,[20] we estimate that our reported droplet sizes are accurate to ap-

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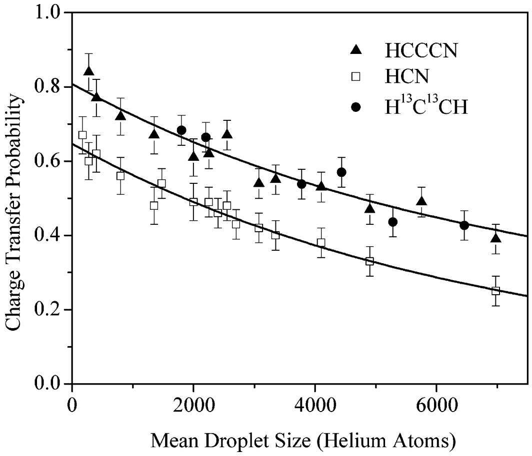

Figure 4. A plot of the experimentally measured charge-transfer probabilities (CTP) for HCN, HCCCN, and $H^{13}C^{13}CH$, over a range of mean droplet sizes. The solid lines are quadratic fits to the data and are meant only to show the general trends.

proximately 10% for droplets larger than 1400 atoms (including the atoms evaporated during pickup). For smaller droplets, we rely on the extrapolation of the scaling laws, so that the mean droplet sizes are likely less well determined.

There are several surprising aspects of the data in Figure 4 that are important to point out. First, the CTPs for HCCCN and HCCH are the same within the experimental uncertainty, while those of HCN are significantly lower. Clearly, the size of the molecule is not the dominant issue, given the CTP of HCCH is comparable to the CTP of the significantly "larger" HCCCN. Similarly, there is no obvious correlation between the relative CTPs and the polarity of the molecules, given that both HCN and HCCCN have large dipole moments, while HCCH is nonpolar. The other surprising result is that a smooth extrapolation of the data in Figure 4 to zero droplet size does not give CTPs of unity, as one would expect from the charge-hopping mechanism discussed above. Indeed, these results are in contrast with earlier studies of the charge transfer to NO in helium,[13] where the data did extrapolate to unity for small droplet sizes. The present results are particularly surprising given that gas-phase afterglow studies indicate charge transfer from He^+ to a wide variety of molecules proceeds with gas kinetic cross sections.[37]

In an attempt to explain the above data, we explored the possibility that the presence of the dopant significantly affects the charge-hopping process in the helium droplet. This seems reasonable given the strong interaction between the permanent electrostatic moments of the molecule and the He^+ charge. Since these interactions can be either attractive or repulsive, it is possible that a He^+ produced near the positive end of a molecular dipole would be pushed away from the molecule, rather than attracted to it, which would clearly reduce the CTP for the molecule and might account for the observed trends. Accordingly, we calculated the potential energy of a unit positive point charge interacting with the molecules HCN, HCCCN, HCCH, and NO at the MP2/6-311G** level of theory using the Molpro suite of programs.[38] The resulting potential energy surfaces are shown in Figure 5, where the center of mass of each molecule has been placed at the origin of the Cartesian coordinate system. The spacing between the contours in these potentials is 500 cm^{-1}, illustrating that the corresponding interactions are quite large. For example, the potential for the HCN (Figure 5a) is highly repulsive (dotted contours) near the H atom, (the positive end of the molecular dipole) and the potential is strongly attractive (solid contours) near the N atom.

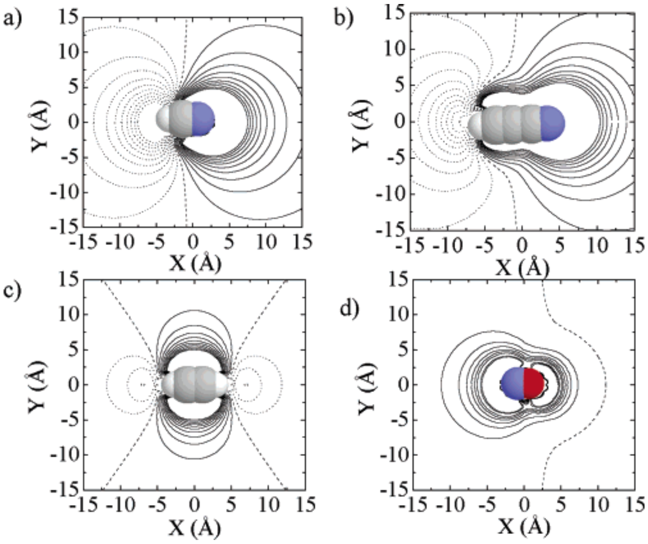

Figure 5. Potential energy surfaces corresponding to a point positive charge interacting with (a) HCN, (b) HCCCN, (c) $H^{13}C^{13}CH$, and (d) NO. In each case, dotted (solid) lines represent regions of positive (negative) energy. The dashed lines show the zero energy contour. The contour spacing is 500 cm^{-1}.

When considering the effects of this potential on the charge-transfer mechanism, we note that the time between charge "hops" is estimated to be only 20 fs,[18] which means that the dopant does not have time to reorient under the influence of this potential. Thus, if electron impact ionization happens to produce a helium cation in a repulsive portion of the potential, for instance, near the H atom of HCN, the charge will experience a repulsive interaction. Although there is no barrier on the potential surface preventing the charge from taking a curved path around the molecule to the attractive region of the potential, the number of charge hops required to do so will be greater, thus increasing the likelihood that the charge will form a He_n^+ ion before reaching the dopant molecule. In essence, there is an "excluded volume" in the droplet where newly formed helium cations are repelled from the dopant and thus are unable to

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transfer charge to it. Such a mechanism would explain the fact that the CTPs do not extrapolate to unity, given that this effect persists to the very smallest droplets.

Further support for this charge-steering model is found upon comparing the relative "excluded volumes" for the various molecules in Figure 5. For example, although the potentials for HCN and HCCCN are both repulsive at the H ends of the molecules, the excluded volume is considerably smaller for HCCCN. This is due to the relatively large polarizability of HCCCN perpendicular to the molecular axis[39] compared to that of HCN.[39] The fact that the excluded volume for HCCCN is smaller than that for HCN is consistent with the observation that the CTP for HCCCN is larger than that for HCN at all droplet sizes.

As noted above, previous studies of charge transfer to NO in helium[13] suggested that the CTP approaches unity in the limit of zero droplet size. This is also consistent with the above picture, given that the associated charge−molecule interaction potential is attractive at all angles for NO (Figure 5d). Finally, the potential for HCCH (Figure 5c) reflects the fact that this system is nonpolar but has a significant quadrupole moment.[39] Although it is not immediately apparent from inspection of the potentials in Figure 5, a quantitative analysis reveals that HCCH and HCCCN have approximately the same excluded volume, in agreement with the fact that the experimentally determined CTPs for these two molecules are the same.

We now consider the steps required to turn the qualitative comparisons given above into a quantitative analysis of the experimental and theoretical results. To obtain a quantitative estimate of the excluded volumes for these systems, we used a Monte Carlo procedure to model the motion of the charge inside the droplet. Seong and co-workers[40] have developed a quantum mechanical description of the charge migration process in which the charge is described by a wave packet, initially localized on a single helium atom, which then propagates through the droplet (possibly delocalizing over several helium atoms) until either He_n^+ or the molecular ion is formed. Since the short-time motion of a wave packet in a potential is often quite similar to the trajectory of a classical particle on the potential,[41] we can use a classical approach to approximate the motion of the charge. We begin by placing a dopant molecule at the center of a droplet of a given size. The droplet is assumed to be spherical and a cavity of the correct size is provided to accommodate the molecule, on the basis of the results of Whaley and co-workers.[42] A positive charge is then placed on a randomly chosen helium atom and allowed to hop from one helium atom to another, with the direction of each hop determined by the gradient of the potential at that point. This potential includes the interaction between the ion and the helium solvent, calculated using the results of Lehmann,[43] as well as the ion−dopant potential discussed above. The latter interactions dominate when the charge is close to the dopant molecule, while charges near the surface of a large droplet experience a significant interaction because of the helium solvent, which pulls the charge toward the droplet center. In the previous studies of Janda and co-workers[15] with argon as the dopant, the charge-hopping process was directed by weighting a hop in a randomly chosen direction by the charge-induced dipole interaction of the He^+−Ar potential and the effects of the helium solvent. In the present case, where the ion−dopant interactions are much stronger because of the large dipole or quadrupole moments of the molecular dopants, this weighting factor is overwhelmingly in favor of the charge moving directly along the path leading downhill on the overall potential surface. Although test runs with a Boltzmann weighting factor were carried out, the results were indistinguishable from those obtained from this direct hopping mechanism. As a result, all of the results presented here were obtained using the latter approach. The motion of the charge continues until the charge either reaches the dopant molecule, at which point charge transfer is assumed to occur, or a specified number of "hops" is exceeded, in which case it is assumed that a He_n^+ ion is formed and desolvated.[19] Several thousand simulations were run for a range of droplet sizes, to ensure convergence of the calculation of the average CTP. The assumption that the dopant molecule is at the center of the droplet was tested using simulations based upon a radial distribution function from Lehmann[44] and did not significantly affect the results. The length of a hop[18] was fixed at 3.1 Å, although it is really only the product of this length and the number of hops that is significant, reflecting the lifetime of the He^+ charge in the droplet.

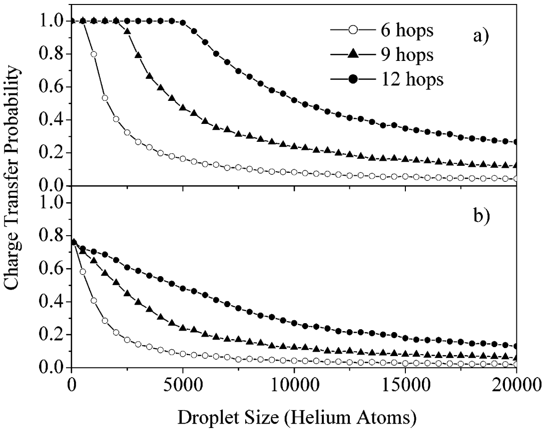

Figure 6. Charge-transfer simulations for monodispersed droplets, allowing 6, 9, and 12 hops before He_n^+ formation. In (a) the ion−dopant potential is turned off and the ion-droplet potential guides the charge toward the dopant, located at the center of the droplet. In (b) the ion−dopant potential for HCN is included and the effects of the excluded volume are evident (see text).

Figure 6a shows a series of CTP calculations (for different numbers of allowed hops) versus droplet size, where the charge−dopant interaction has been switched off and the ion moves directly toward the center of the droplet (namely, toward the dopant molecule) under the influence of the solvent potential.[43] In this case, all of the curves approach unity at zero droplet size, as one would expect from a purely attractive potential. In fact, the charge-transfer probability remains unity (as the droplet size increases) until the radius of the droplet is greater than the average hopping range of the He^+ ion, at which point the CTP decreases smoothly. In the limit of an infinite

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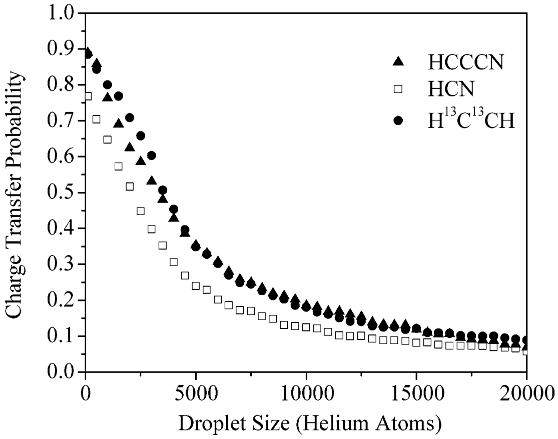

Figure 7. Charge-transfer simulations for HCN, HCCCN, and $H^{13}C^{13}CH$ as a function of the droplet size. In each case, the number of hops is fixed at nine. In agreement with the experimental data, the CTP curves for HCCCN and $H^{13}C^{13}CH$ are almost coincident, while HCN is significantly lower.

number of allowed hops, the CTP would remain unity for all droplet sizes, indicative of the fact that under these circumstances, the charge would eventually find the molecule.

Figure 6b shows a second set of simulations, with the ion−molecule potential (in this case for HCN) included. At zero droplet size, the curves converge to 0.76, indicative of the excluded volume imposed by the ion−dopant interaction. The implication is that 24% of the droplet volume lies in a sufficiently repulsive part of the potential to prevent the charge from reaching the HCN molecule. In addition, the plateaus seen in Figure 6a are missing, since the charges no longer move in straight paths toward the center of the droplets. Once again, the CTPs decrease more rapidly when the allowed number of hops is small.

Figure 7 shows CTPs calculated for the three molecules considered here, on the basis of the ab initio potentials given in Figure 5. In these cases, the number of hops is fixed at nine and the droplets are assumed to be monodispersed. As anticipated above, the calculated CTPs are nearly coincident for HCCCN and HCCH, while the corresponding results for HCN are significantly lower, again in qualitative agreement with the experimental observations. It is also evident from Figure 7 that the slopes of the curves for the three molecules are rather similar, at least for droplets smaller than 10 000 atoms, which is also in good qualitative agreement with the experimental results shown in Figure 4. Once again, we wish to emphasize that although the migration of the charge inside the droplet is a quantum mechanical process, the two most important aspects of the migration on the associated potential energy surfaces (that some regions of the potential are repulsive to the charge and that the charge can only move a limited distance before He_n^+ formation occurs) are represented in our classical approximation.

To make quantitative comparisons between the experimental and theoretical results, it is necessary to average the curves shown in Figure 7 over a log-normal distribution of droplet sizes. Although the effects of this averaging are rather weak for small droplets, they are relatively more important with increasing droplet size, since the width of the distributions varies as $(\langle N \rangle)^{1/2}$.[24] Given that the OSMS data corresponds to droplets containing a single dopant molecule, we must also weight the results according to the probability that a particular droplet size will pickup a single molecule, a process well-described by Poissonian statistics.[7] The distribution is also weighted according to the sensitivity of mass spectrometer signal to various droplet sizes. As noted above, the optically selected mass spectra correspond to the reduction in droplet ionization cross section because of the laser-induced evaporation of helium atoms (approximately 600 atoms) from the droplet. Using the results from a previous investigation[24] which show that the ionization cross section scales as $N^{2/3}$, we can quantitatively account for the reduction. We also accounted for the fact that OSMS spectra are less sensitive to droplets with fewer than 600 helium atoms, namely, fewer atoms than typically evaporated by the laser. Since all of these effects are well understood, the corresponding correction factors do not introduce any adjustable parameters to the model.

Finally, previous infrared studies of HCN,[45] HCCH,[26] and HCCCN[46] from our group have shown that the corresponding spectra broaden as the droplet size decreases. This inhomogeneous broadening influences the efficiency with which the molecules can be pumped by a laser, given that the laser bandwidth is considerably narrower than the inhomogeneous line width of the solvated molecules. This effect is only important for the very smallest droplets and is well characterized from our previous studies. A correction factor was included to account for this effect. Once again, there are no adjustable parameters in any of these weighting factors, since they are all well determined from previous experimental studies. Finally, there are really two contributions to the OSMS signals observed here. The main contribution is from the laser-induced decrease in the ionization cross section of the droplets, resulting from the evaporation of several hundred helium atoms. A smaller effect is the corresponding increase in the CTP to the molecule, because the droplets are now slightly smaller. The latter effect is completely absent in the smallest droplets, which completely evaporate upon laser excitation, and is small for the larger droplets, although it can result in a slight change in the slope of the lines in Figure 4. As a result, the number of hops determined from the fit to the data should be considered a lower limit (which is not too severe a problem, given the difficulties associated with the quantitative physical interpretation of this quantity, as discussed below).

A single parameter is left to fit the calculated CTPs to the experimental results, namely, the number of allowed hops. Figure 8 shows a comparison between the experiment and theory, on the basis of nine hops in each case. The agreement is excellent, giving support to the mechanism discussed above. It is interesting to compare our estimate of the number of hops for the systems studied here with the previous estimates for neon, argon, and xenon, which are in the range of three to four. Once again, the hop number is our way of quantifying the time the He^+ has to find the molecule before it spontaneously forms He_n^+. Nevertheless, the implication seems to be that the He^+ moves further when the ion−dopant interaction is stronger. This makes some sense given that the rate of hopping (the ion velocity) is likely to be greater in a strongly interacting system. In the wave packet description mentioned above,[40] this would correspond to acceleration of the wave packet as it moves toward lower energy areas of the potential.

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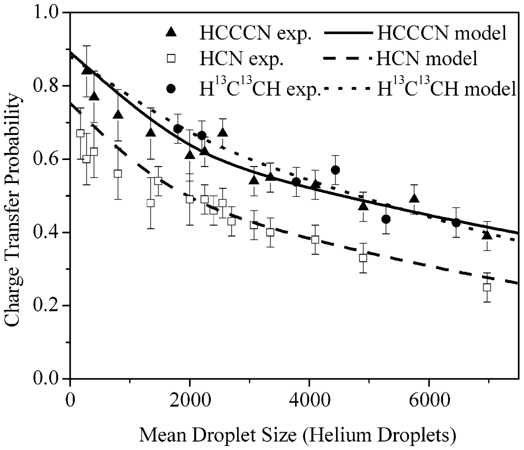

Figure 8. A plot showing the comparison between the experimental data and results of model calculations, which take into account the distribution of droplet sizes (see text). In the model, the only adjustable parameter was the number of allowed hops. Nine hops is found to give the best agreement with the experimental data.

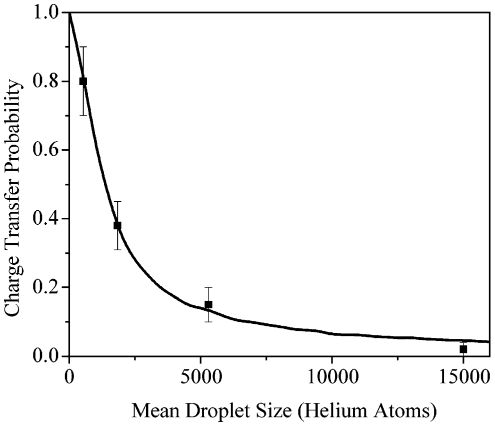

Figure 9. A plot showing a comparison between the experimental results of Janda and co-workers[13] for NO in helium and the results of the model calculations presented here. In this case, the curves extrapolate to zero since the ion−NO potential is attractive at all angles, so that the excluded volume is zero in this case (see text).

Using the ion−dopant potential calculated here for NO, we have also carried out a reanalysis of the corresponding data of Janda and co-workers.[13] Their original analysis of these data was based on a model that was later shown to overestimate the number of hops,[15] namely, 70. The fitted curve shown in Figure 9, along with the experimental data for NO,[13] was obtained using the same method as described above, with the exception that the droplet size distribution was weighted solely by the total ionization cross section of the droplet,[24] given that this data was taken from the full mass spectrum rather than the infrared selected results presented above. This best fit yields seven hops, intermediate between the value obtained from the HCN, HCCCN, and HCCH data and those reported previously for the rare gases. This is completely reasonable given the relative magnitudes of the ion−dopant interactions in all of these cases. As expected from the fact that NO does not have an excluded volume, the calculated and experimental results extrapolate to unity at small droplet sizes.

Conclusion

We have measured the charge-transfer probabilities between He^+ and a series of molecular dopants, solvated in helium nanodroplets. The results are rather directly extracted from the experimental data obtained using a new form of optically selected mass spectrometry (OSMS) to separate out the various contributions to the overall helium nanodroplet mass spectrum. This method combines high-resolution infrared laser spectroscopy with helium droplet mass spectrometry and provides a means of obtaining data that is free from the effects of droplet contamination. This data shows that the charge-transfer probabilities depend on the identity of the dopant molecule and are explained by a model in which the migrating charge is steered by the ion−dopant potential. While a He^+ ion produced by electron impact near the negative end of a molecular dipole will be directly attracted to the molecule and thus have a large probability for charge transfer, ions formed near the positive end of the molecule will be repelled and thus are more likely to form a He_n^+ ion. Similar behavior is observed in the case of acetylene, where the charge steering is now the result of the ion−quadrupole interaction.

The results presented above give further insights into the nature of the charge migration in helium nanodroplets. The ab initio potential surfaces presented here provide a quantitative description of the charge-transfer process. This charge steering is particularly interesting in view of previous studies that have shown that the fragmentation of peptides[47] and other large organic molecules[48,49] is dependent upon the initial site where ionization occurs. Thus, even though electron impact ionization is normally considered one of the least sophisticated ionization methods, when combined with the helium nanodroplets technique, it can afford unusual control over the way in which the charge is delivered to the molecule. It is interesting to consider the study of different isomers of a given system that have quite different dipole (or higher electrostatic) moments, which could be used to steer the charge to different sites on the molecule, thus modifying the corresponding fragmentation pattern. Such a scheme could be useful in obtaining isomer selective mass spectra for such systems. In addition, helium nanodroplets can be used to assemble a variety of interesting complexes,[2,31] providing us the exciting prospect of manipulating the ionization site by controlling the direction of the electrostatic moments of the complex, for example, steering the charge to a particular functional group of the molecule. In fact, these effects are now being considered as mechanisms for explaining the anomalous enhancement of one of the fragmentation channels of triphenylmethanol in helium nanodroplets.[20] Further studies on more complex molecules will be needed to explore the full potential of this approach.

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