J|A|C|S
ARTICLES

Published on Web 09/20/2010

IR Spectroscopy of Molecular Ions by Nonthermal Ion Ejection from Helium Nanodroplets

Szymon Smolarek,[†] Nils B. Brauer,[‡] Wybren J. Buma,[†] and Marcel Drabbels*[,‡]

University of Amsterdam, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands, and
Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne
(EPFL), CH-1015 Lausanne, Switzerland

Received April 23, 2010; E-mail: marcel.drabbels@epfl.ch

Abstract: Infrared spectroscopy provides a means to determine the intrinsic geometrical structures of molecules. Here we present a novel spectroscopic method that uses superfluid helium nanodroplets to record IR spectra of cold molecular ions, in this particular case aniline cations. The method is based on the detection of ions that are ejected from the helium droplets following vibrational excitation of these ions. We find that spectra can be recorded with a high sensitivity and that they exhibit only a small matrix shift. The widths of the individual transitions depend on the excited vibrational level and are thought to be related to the interaction of the ion with the surrounding helium solvent shells.

1. Introduction

The function of a molecule is intimately related to its structure. Accordingly, in the quest for a better understanding of molecular function, the development of spectroscopic methods to elucidate molecular structures increasingly takes central stage. The amount of detail that can be derived from spectra depends on the experimental conditions, most notably on the temperature of the sample and the intermolecular interactions a molecule experiences. Helium nanodroplets provide in this respect an almost ideal matrix.[1,2] For neutral molecules, helium nanodroplet spectroscopy thus has led to important discoveries related to the structure of key molecular systems[3−6] and has provided insight into the mechanisms underlying chemical reactions.[7,8]

Under real-life, aqueous conditions, many molecular systems are actually present in a protonated or deprotonated form. Although significant progress has been made in the study of such ionic systems by storing them in cryogenically cooled ion traps,[9] their spectroscopic exploration is still in its infancy compared to the level of sophistication that has been reached for neutrals. The use of helium droplets as a cryogenic matrix could potentially solve many of the technical challenges associated with recording high-resolution spectra of cold molecular ions. There are extensive reports in the literature on the formation of cations and anions, both intrinsic and extrinsic, using He droplets.[10−24] However, the feasibility of creating ion-containing helium droplets has only recently been demonstrated.[25,26] Unfortunately, spectroscopic studies have remained out of reach because techniques to study ion-doped helium droplets with the required sensitivity are still lacking. Here, we present a novel approach that meets these demands and that finds its roots in the nonthermal cooling dynamics of excited molecular ions in helium droplets.

[†] University of Amsterdam.
[‡] Ecole Polytechnique Fédérale de Lausanne.

(1) Scoles, G.; Lehmann, K. K. *Science* **2000**, *287*, 2429.
(2) Toennies, J. P.; Vilesov, A. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 2622.
(3) Nauta, K.; Miller, R. E. *Science* **1999**, *283*, 1895.
(4) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.
(5) Dong, F.; Miller, R. E. *Science* **2002**, *298*, 1227.
(6) Choi, M. Y.; Miller, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 7320.
(7) Nauta, K.; Moore, D. T.; Stiles, P. L.; Miller, R. E. *Science* **2001**, *292*, 481.
(8) Gutberlet, A.; Schwaab, G.; Birer, O.; Masia, M.; Kaczmarek, A.; Forbert, H.; Havenith, M.; Marx, D. *Science* **2009**, *324*, 1545.
(9) Rizzo, T. R.; Stearns, J. A.; Boyarkin, O. V. *Int. Rev. Phys. Chem.* **2009**, *28*, 481.
(10) Farnik, M.; Toennies, J. P. *J. Chem. Phys.* **2005**, *122*, 014307.
(11) Fröchtenicht, R.; Henne, U.; Toennies, J. P.; Ding, A.; Fieber-Erdmann, M.; Drewello, T. *J. Chem. Phys.* **1996**, *104*, 2548.
(12) Lewerenz, M.; Schilling, B.; Toennies, J. P. *J. Chem. Phys.* **1995**, *102*, 8191.
(13) Scheidemann, A.; Schilling, B.; Toennies, J. P. *J. Phys. Chem.* **1993**, *97*, 2128.
(14) Buchenau, H.; Toennies, J. P.; Northby, J. A. *J. Chem. Phys.* **1991**, *95*, 8134.
(15) da Silva, F. F.; Denifl, S.; Mark, T. D.; Doltsinis, N. L.; Ellis, A. M.; Scheier, P. *J. Phys. Chem. A* **2010**, *114*, 1633.
(16) da Silva, F. F.; Bartl, P.; Denifl, S.; Mark, T. D.; Ellis, A. M.; Scheier, P. *Chem. Phys. Chem.* **2010**, *11*, 90.
(17) Schobel, H.; Dampc, M.; da Silva, F. F.; Mauracher, A.; Zappa, F.; Denifl, S.; Mark, T. D.; Scheier, P. *Int. J. Mass spectrom.* **2009**, *280*, 26.
(18) Mauracher, A.; Schobel, H.; da Silva, F. F.; Edtbauer, A.; Mitterdorfer, C.; Denifl, S.; Mark, T. D.; Illenberger, E.; Scheier, P. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8240.
(19) Jaksch, S.; Mahr, I.; Denifl, S.; Bacher, A.; Echt, O.; Mark, T. D.; Scheier, P. *Eur. Phys. J. D* **2009**, *52*, 91.
(20) Denifl, S.; Mahr, I.; da Silva, F. F.; Zappa, F.; Mark, T. D.; Scheier, P. *Eur. Phys. J. D* **2009**, *51*, 73.
(21) Callicoat, B. E.; Förde, K.; Ruchti, T.; Janda, K. C. *J. Chem. Phys.* **1998**, *108*, 9371.
(22) Ruchti, T.; Förde, K.; Callicoat, B. E.; Ludwigs, H.; Janda, K. C. *J. Chem. Phys.* **1998**, *109*, 10679.
(23) Ruchti, T.; Callicoatt, B. E.; Janda, K. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4075.
(24) da Silva, F. F.; Waldburger, P.; Jaksch, S.; Mauracher, A.; Denifl, S.; Echt, O.; Mark, T. D.; Scheier, P. *Chem.*—*Eur. J.* **2009**, *15*, 7101.
(25) Claas, P.; Mende, S. O.; Stienkemeier, F. *Rev. Sci. Instrum.* **2003**, *74*, 4071.
(26) Kupser, P.; Bierau, F.; Meijer, G.; von Helden, G. *Phys. Rev. Lett.* (in press).

10.1021/ja1034655

2. Experimental Approach

For the experiments, a beam of helium nanodroplets is formed by introducing helium at a pressure of 30 bar into a vacuum via a 5 μm nozzle that is cooled to cryogenic temperatures.[27,28] The mean droplet size can be readily varied from 1000 to 20 000 helium atoms by changing the temperature of the nozzle.[29−31] The beam of helium nanodroplets is directed into another vacuum chamber in which aniline vapor is present at a partial pressure in the range of $10^{-5}-10^{-6}$ mbar. Here, the droplets pick up by collision on average less than one aniline molecule. For experiments on aniline dimers, the partial pressure of aniline is increased substantially, leading to the pickup of on average two aniline molecules by the droplets. Via a differential pumping stage, the doped droplets enter a time-of-flight mass spectrometer with velocity map imaging capabilities.[32] At the center of the spectrometer, the droplet beam is crossed by UV radiation generated by frequency-doubling the output of a Nd:YAG pumped dye laser. By tuning the frequency of the excitation light to 34 100 cm^{-1} so as to match the maximum in the absorption of the $S_1 \leftarrow S_0$ band origin in helium droplets, the embedded aniline molecules are ionized via a resonance-enhanced two-photon absorption process.[33] In order to maximize the ion yield, the UV beam is weakly focused by a lens with a focal length of 40 cm. Although a large number of ions are ejected from the droplets in the photoionization process, approximately half of the ions created remain solvated in the helium droplets (*vide infra*). After these solvated ions are allowed to equilibrate with the cold helium environment for a period of up to several hundreds of nanoseconds—i.e., long on the time scale of vibrational cooling[33−35]—the ions are exposed to IR radiation. Radiation at 3 μm with an energy of up to 1 mJ/pulse is generated by difference frequency mixing the output of an injection seeded Nd:YAG laser with the output of a tunable dye laser in a $LiNbO_3$ crystal. IR radiation at 1.5 μm with pulse energies up to 4 mJ is produced by Raman shifting the output of a tunable dye laser in high-pressure hydrogen gas. The IR radiation is weakly focused in order to match the beam size of the UV radiation. Following absorption of the IR radiation by the ions, the photon energy is efficiently transferred to the helium environment, leading to the formation of bare or only partially solvated aniline ions. Most of the experiments reported here are performed with a time delay of 200 ns between the UV and IR laser pulses. At this delay, the aniline ions resulting from the IR excitation are clearly resolved in the time-of-flight mass spectrum from aniline$^+$−He$_n$ complexes formed by UV excitation. By monitoring the number of aniline ions impinging on the detector at the appropriate arrival time as a function of laser frequency, background-free IR excitation spectra can be recorded. In addition, it is possible to determine the velocity distributions of the ions from two-dimensional images recorded by the imaging setup.

3. Results and Discussion

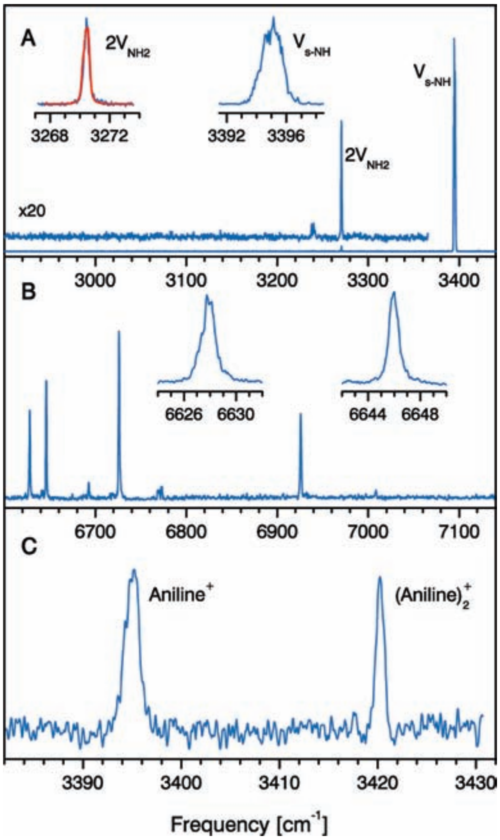

Figure 1. Infrared spectra of aniline ions in helium droplets. (A) IR excitation spectrum of aniline ions in liquid helium nanodroplets, recorded by monitoring the appearance of bare aniline ions. The insets show a detailed view of the symmetric NH-stretching vibration ($\nu_{\text{s-NH}}$) and the NH$_2$-scissoring overtone ($2\nu_{NH_2}$) band, together with the simulated spectrum (red line). (B) Excitation spectrum in the NH-stretch overtone region. Detailed views of two intense bands are presented in the insets. (C) IR spectrum of the aniline dimer cation by monitoring the appearance of aniline$_2^+$ dimers. The signal corresponding to the aniline monomer is caused by the use of a rather wide mass gate that allows detection aniline$_2^+$−He$_n$ ($22 < n < 37$) complexes besides aninile$_2^+$ dimers.

3.1. Spectroscopy. The fact that vibrational excitation of aniline ions solvated in helium droplets leads to the formation of bare aniline ions without any helium atoms attached allows for a background-free and thus sensitive detection of IR absorptions by the embedded ions. Figure 1A depicts a spectrum covering the frequency region of 2900−3450 cm^{-1} that exhibits a signal-to-noise ratio of more than 1000. Two transitions can be readily discerned in this spectrum. The strong transition at 3395.1 cm^{-1} can be assigned to the symmetric NH-stretch ($\nu_{\text{s-NH}}$). The observed transition frequency for this band compares well with the gas-phase value of 3393 cm^{-1}[36] and is identical to that determined using the Ar-tagging technique.[37] Although spectra of aniline ions in a cryogenic matrix have been reported, no data are available for this specific transition.[38] In the ionic aniline−Ar complex, the NH$_2$-scissoring vibration is found at 1635 cm^{-1}.[39] The transition observed here at 3270.5 cm^{-1} has therefore been assigned to its overtone ($2\nu_{NH_2}$).[40] In addition, a very weak absorption is observed around 3240 cm^{-1}, which we tentatively assign to the combination band of the NH$_2$-scissoring vibration and the 8a ring vibration.[41] The high sensitivity of

---

(27) Loginov, E.; Drabbels, M. *J. Phys. Chem. A* **2007**, *111*, 7504.
(28) Braun, A.; Drabbels, M. *J. Chem. Phys.* **2007**, *127*, 114303.
(29) Lewerenz, M.; Schilling, B.; Toennies, J. P. *Chem. Phys. Lett.* **1993**, *206*, 381.
(30) Harms, J.; Toennies, J. P.; Dalfovo, F. *Phys. Rev. B* **1998**, *58*, 3341.
(31) Knuth, E.; Schilling, B.; Toennies, J. P. In *Proceedings of the 19th International Symposium on Rarefied Gas Dynamics*; Lord, G., Harvey, J., Eds.; Oxford University Press: London, 1995; p 270.
(32) Eppink, A. T. J. B.; Parker, D. H. *Rev. Sci. Instrum.* **1997**, *68*, 3477.
(33) Loginov, E.; Rossi, D.; Drabbels, M. *Phys. Rev. Lett.* **2005**, *95*, 163401.
(34) Radcliffe, P.; Przystawik, A.; Diederich, T.; Doppner, T.; Tiggesbaumker, J.; Meiwes-Broer, K. H. *Phys. Rev. Lett.* **2004**, *92*, 173403.
(35) Lehnig, R.; Slenczka, A. *J. Chem. Phys.* **2003**, *118*, 8256.
(36) Honda, M.; Fujii, A.; Fujimaki, E.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2003**, *107*, 3678.
(37) Nakanaga, T.; Ito, F.; Miyawaki, J.; Sugawara, K.; Takeo, H. *Chem. Phys. Lett.* **1996**, *261*, 414.
(38) Gee, C.; Douin, S.; Crepin, C.; Brechignac, P. *Chem. Phys. Lett.* **2001**, *338*, 130.
(39) Piest, H.; von Helden, G.; Meijer, G. *J. Chem. Phys.* **1999**, *110*, 2010.
(40) Solca, N.; Dopfer, O. *Eur. Phys. J. D* **2002**, *20*, 469.
(41) Song, X. B.; Yang, M.; Davidson, E. R.; Reilly, J. P. *J. Chem. Phys.* **1993**, *99*, 3224.

the method, which exceeds that of other methods used to record IR spectra of aniline ions by almost 2 orders of magnitude, allows for the detection of the hitherto unobserved overtone transitions of the NH-stretching vibrations in the 1.5 μm region (Figure 1B). Analogous to neutral aniline,[42] a total of six transitions can be identified due to a Fermi resonance between the NH-stretching and the NH_2-scissoring overtone vibrations. Despite the excellent signal-to-noise ratio of the spectra, no resonances are observed in the 3000−3200 cm^{-1} region that can be attributed to CH-stretch vibrations of the aniline cation. This confirms the results of calculations that predict that the absorption cross sections for the CH-stretch vibrations are at least 2 orders of magnitude smaller than those of the corresponding NH vibrations.[39,43] The observed transition frequency of $\nu_{\text{s-NH}}$, which is found to be independent of the helium droplet size, implies a matrix shift of $+2$ cm^{-1}.[36] A matrix shift of this magnitude seems surprising since it is only slightly larger than typical shifts observed for neutrals.[2] While neutrals are surrounded by rather fluxional helium solvation layers,[44] highly structured solvation shells with densities exceeding that of solid helium are formed around ions.[24,45−47] One would expect the enhanced helium density to lead to a substantial blue shift of the vibrational frequencies. That only a small shift is observed indicates that either the effect of electrostriction on the transition frequencies is not significant or that, like for neutrals, the blue shift is largely compensated by the red shift originating from attractive electrostatic induction interactions.[48] On the other hand, it should be noted that shifts of similar magnitude have been observed for IR transitions of aniline cations in an argon matrix.[38]

Closer inspection of the two main bands in the 3 μm region spectrum reveals that the widths of the transitions differ significantly, 0.4 cm^{-1} for the NH_2-scissoring overtone vs 1.6 cm^{-1} for the NH-stretch vibration (inserts Figure 1). Moreover, the overall line shape of the NH_2-scissoring overtone band is found to be symmetric, while the line shape of the NH-stretch vibration is asymmetric toward lower frequency. Since these line shapes are independent of the IR intensity, even when this is varied over 3 orders of magnitude, we conclude that the difference in line width is intrinsic and not caused by saturation effects. The contour of the NH_2-scissoring overtone band can be reproduced by rotational band contour simulations (see Supporting Information). The best agreement between the simulated rotational contour and observed line shape is obtained assuming a rotational temperature of 0.38 K, a Lorentzian line width for the individual rovibrational transitions of 0.25 cm^{-1}, and rotational constants that are a factor of 9 smaller than the corresponding gas-phase values (Figure 1). This rotational temperature indicates that, upon their creation, the ions are cooled to the equilibrium temperature of the droplets. The relatively large line width of individual rovibronic transitions and the strong reduction in rotational constants are compatible with the formation of strongly bound solvation layers around the ion. The relatively strong coupling between the ion and the helium will most likely lead to an increase of the moment of inertia and a faster relaxation of the vibrationally excited level.

While an excellent agreement between the simulated band contour and the observed line profile can be obtained for the NH_2-scissoring overtone, this is not the case for the fundamental transition of the NH-stretch. Even when allowing for the possibility that the band might be a superposition of two transitions originating from a resonance between the NH-stretching vibration and a combination band, no satisfactory agreement could be obtained. Hence, it appears more plausible that the line width and asymmetry are primarily determined by interactions of the ion with the helium environment, a conclusion that is corroborated by an analysis of the line shapes in the 1.5 μm region. These bands are all significantly broader than 0.4 cm^{-1} and, except for the transition at 6646 cm^{-1}, slightly asymmetric. Even though their overall width can be reproduced fairly well assuming a Lorentzian line width for individual rovibrational transitions of 0.6 cm^{-1}—indicating that vibrational relaxation is enhanced compared to the fundamental levels—their asymmetry cannot be reproduced.

The fact that line broadening of this type is not observed for similar vibrational transitions of neutral species in liquid helium suggests that it might be related to the charge of the embedded molecule. It is not unlikely that the ions are surrounded by helium solvation shells that have geometrically different configurations but similar energies. Moreover, spectroscopic studies on complexes of aniline ions with argon have revealed line splittings due to the presence of several low-energy structures.[40,49] *Ab initio* calculations accompanying those experiments indicate that the frequency of the NH-stretching modes depends strongly on the structure of the complex, while this is not the case for the NH_2-scissoring mode.[40] In view of the analogy with the results on aniline$^+$−argon complexes, we propose that line broadening of the symmetric NH-stretching vibrations originates in the existence of geometrically different helium solvation shells surrounding the aniline ions.

The conclusion that the line width is possibly related to helium solvation structures surrounding the ion is exciting, as it could potentially offer a novel means to map out charge distributions of ions and thereby obtain information on their geometrical structure. For larger molecular ionic systems, the charge is in general localized, and structured helium solvation shells are expected to form only around the charged part of the molecule. Only those vibrations that involve atoms interacting with these solvation shells are thus prone to exhibit broadened resonances. Experiments on the aniline dimer are in line with this concept. From gas-phase experiments, it is known that, in the aniline dimer cation, the charged aniline is hydrogen-bonded to the nitrogen atom of the neutral.[50,51] As a result, the interaction between the NH-stretching vibrations of the aniline cation and the helium solvation shells is modified. Figure 1C shows the corresponding IR absorption spectrum recorded in helium droplets. Due to the use of a rather wide mass gate, which leads to detection of not only the aniline$_2^+$ dimer but also aniline$^+$−He$_n$ ($22 < n < 37$) complexes, the spectrum reveals contributions of both the aniline ion and the aniline$_2^+$ dimer.

---

(42) Fehrensen, B.; Hippler, M.; Quack, M. *Chem. Phys. Lett.* **1998**, *298*, 320.
(43) Wojciechowski, P. M.; Zierkiewicz, W.; Michalska, D.; Hobza, P. *J. Chem. Phys.* **2003**, *118*, 10900.
(44) Kwon, Y.; Huang, P.; Patel, M. V.; Blume, D.; Whaley, K. B. *J. Chem. Phys.* **2000**, *113*, 6469.
(45) Nakayama, A.; Yamashita, K. *J. Chem. Phys.* **2000**, *112*, 10966.
(46) Marinetti, F.; Bodo, E.; Gianturco, F. A. *Chem. Phys. Chem.* **2007**, *8*, 93.
(47) Di Paola, C.; Bodo, E.; Gianturco, F. A. *Eur. Phys. J. D* **2006**, *40*, 377.
(48) Callegari, C.; Lehmann, K. K.; Schmied, R.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 10090.
(49) Nakanaga, T.; Ito, F. *Chem. Phys. Lett.* **2002**, *355*, 109.
(50) Nakanaga, T.; Chowdhury, P. K.; Ito, F.; Sugawara, K.; Takeo, H. *J. Mol. Struct.* **1997**, *413*, 205.
(51) Ohashi, K.; Inokuchi, Y.; Izutsu, H.; Hino, K.; Yamamoto, N.; Nishi, N.; Sekiya, H. *Chem. Phys. Lett.* **2000**, *323*, 43.

While the resonance at 3395 cm^{-1} has been assigned above to the symmetric NH-stretching vibration of the aniline cation, the resonance at 3420.3 cm^{-1} can be attributed to the free NH-stretching vibration of the cation in the complex.[50] A direct comparison of the two resonances reveals that the width of the dimer resonance, 0.9 cm^{-1}, is significantly less than that of the monomer NH-stretching vibration, 1.6 cm^{-1}, but still broader than that of the NH_2-scissoring overtone. It thus appears that the interaction of the NH-stretch vibration with the helium environment is modified by the presence of the neutral aniline. This seems to suggest that the widths of the transitions are indeed sensitive to the ions' surroundings.

3.2. Ejection Mechanism. In our experiments, IR absorption spectra are recorded by monitoring the number of bare aniline ions as a function of IR frequency. According to the generally accepted model, following the energy transfer from an excited chromophore to the helium bath, the heated droplet will cool by the evaporation of individual helium atoms.[52] In this well-characterized thermal process, every helium atom leaving the droplet takes away its binding energy of ~5 cm^{-1}.[53] Excitation of an NH-stretching vibration around 3400 cm^{-1}, for example, should then lead to the evaporation of about 700 helium atoms. As a result, IR absorptions would only be observable for helium droplets consisting of less than this number of atoms.

However, in recent years, strong indications have been found that cooling of ions in helium droplets is governed by a nonthermal mechanism. This was first discussed by Gspann and Vollmar, who observed the creation of small, charged helium clusters following the electron impact ionization of large helium droplets.[54] In order to explain their observations, these authors suggested that the strong attraction of helium atoms toward the created ion leads to a fast local heating, which results in the ejection of small, charged helium clusters from the large droplet. Later, experiments by Toennies and co-workers revealed that electron impact ionization of helium droplets yields mainly He_2^+ ions.[14] They proposed that, following the ionization of a single helium atom, the charge migrates until it localizes to form He_2^+ ions. The energy released in this process would be dissipated by the helium droplet and lead to the evaporation of a large number of helium atoms, finally yielding bare He_2^+ ions. A few years later, Janda and co-workers showed that the detected He_2^+ ions do not result from a complete thermal evaporation of the droplets but rather from the ejection of the ions from the droplets by an impulsive process.[55,56] Recent experiments by Lewis et al. on the electron impact ionization of molecules in helium droplets have shown that the first several thousand helium atoms leaving the droplets can take away up to 22 cm^{-1} of energy per atom, significantly more than their binding energy, indicative of a nonthermal mechanism.[57,58] Similar results were found in theoretical studies by Bonhommeau et al. on the electron impact ionization of neon clusters in helium droplets.[59,60] In addition, these authors found that a significant fraction of the ions are being ejected from the droplets by a nonthermal process. In all these experiments, the ions are created with a substantial amount of internal energy. This makes it difficult to determine whether ion solvation or vibrational excitation of the ion is responsible for the nonthermal ejection of the ions. Possibly more can be learned about the mechanism from the present study in which cold ions are vibrationally excited.

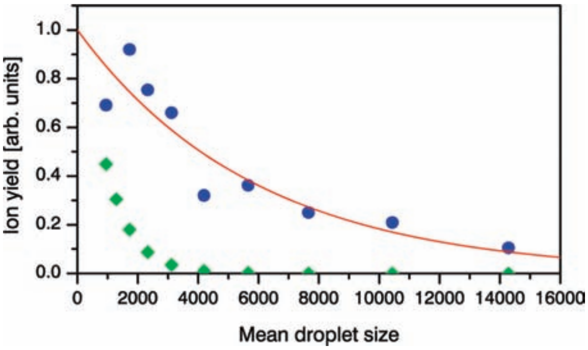

Figure 2. Ion yield (blue circles) following excitation of the symmetric NH-stretch vibration ($\nu_{s\text{-}NH}$) of the aniline cation as a function of the mean size of the ion-doped droplets. The ion yield has been corrected for laser intensities and doped droplet fluxes. The solid line is a fit of an exponential function to the data points. The green diamonds represent the fraction of doped droplets containing less than 700 helium atoms.

In order to find out whether the cooling of vibrationally excited ions is a thermal or nonthermal process, the efficiency by which bare aniline ions are created has been determined as a function of droplet size. For this purpose, the number of bare aniline ions arriving at the detector following excitation of the symmetric NH-stretch ($\nu_{s\text{-}NH}$) vibration has been determined for a range of droplet sizes. Subsequently, these numbers have been corrected for variations in the UV and IR intensities, assuming a linear dependence of the ionization and IR absorption processes on the light intensities. Finally, the results are corrected for the estimated flux of doped droplets at each mean droplet size.[61] The resulting relative ion yields are displayed in Figure 2. As discussed above, the standard evaporative cooling model predicts a sharp cutoff at about 700 helium atoms. However, when comparing the experimental result to the model, the droplet size distribution has to be taken into account.[29] Hence, we have estimated the fraction of doped droplets consisting of less than 700 helium atoms at each mean droplet size. Although time-of-flight mass spectra of solvated ions can be recorded (*vide infra*), they cannot be used to determine this fraction because the detection efficiency of the MCP detector depends strongly on the mass of the impinging ion and the mass range of the spectrometer is limited to 40 000 amu. We therefore have calculated the fraction consisting of less than 700 helium atoms from the estimated size distribution of droplets,[29−31] taking into account that pickup of an aniline molecule leads to the evaporation of approximately 450 helium atoms.[12,43,62] The comparison shown in Figure 2 reveals that the experimental result is clearly at odds with the evaporation model.

---

(52) Brink, D. M.; Stringari, S. *Z. Phys. D: At., Mol. Clusters* **1990**, *15*, 257.

(53) Dalfovo, F.; Lastri, A.; Pricaupenko, L.; Stringari, S.; Treiner, J. *Phys. Rev. B: Condens. Matter* **1995**, *52*, 1193.

(54) Gspann, J.; Vollmar, H. *J. Low Temp. Phys.* **1981**, *45*, 343.

(55) Ovchinnikov, M.; Grigorenko, B. L.; Janda, K. C.; Apkarian, V. A. *J. Chem. Phys.* **1998**, *108*, 9351.

(56) Callicoat, B. E.; Förde, K.; Jung, L. F.; Ruchti, T.; Janda, K. C. *J. Chem. Phys.* **1998**, *109*, 10195.

(57) Lewis, W. K.; Applegate, B. E.; Sztaray, J.; Sztaray, B.; Baer, T.; Bemish, R. J.; Miller, R. E. *J. Am. Chem. Soc.* **2004**, *126*, 11283.

(58) Lewis, W. K.; Bemish, R. J.; Miller, R. E. *J. Chem. Phys.* **2005**, *123*, 141103.

(59) Bonhommeau, D.; Lake, P. T.; Le Quiniou, C.; Lewerenz, M.; Halberstadt, N. *J. Chem. Phys.* **2007**, *126*, 051104.

(60) Bonhommeau, D.; Lewerenz, M.; Halberstadt, N. *J. Chem. Phys.* **2008**, *128*, 054302.

(61) Braun, A. Ph.D. Thesis, EPFL, 2004.

(62) Stringari, S.; Treiner, J. *J. Chem. Phys.* **1987**, *87*, 5021.

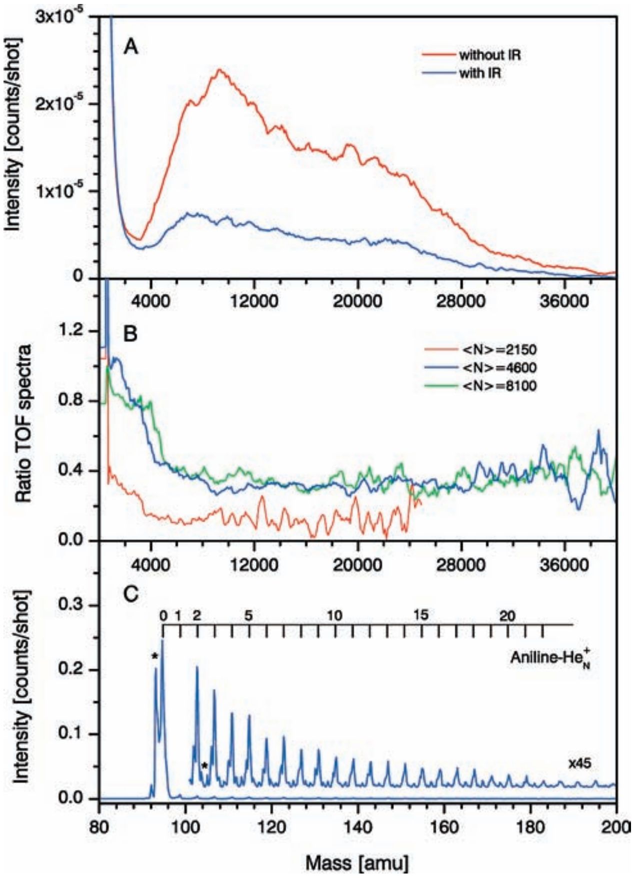

Figure 3. Time-of-flight mass spectra following vibrational excitation of ions. (A) High-mass range of the ion time-of-flight mass spectrum in the presence and absence of IR radiation resonant with the symmetric NH-stretch vibration of the aniline cation embedded in helium droplets consisting on average of 4600 atoms. (B) Ratio of time-of-flight mass spectra with and without resonant IR radiation for helium droplets of different mean droplet sizes. (C) Low-mass range of the time-of-flight mass spectrum following vibrational excitation of the embedded aniline cation. The signals originating from the UV excitation are denoted by asterisks.

More details on the mechanism leading to the formation of bare aniline ions following vibrational excitation can be provided by mass spectrometry and measurements of the speed distributions of the aniline ions. Figure 3A displays time-of-flight mass spectra in the presence and absence of IR radiation resonant with the symmetric NH-stretch vibration of the aniline cation embedded in droplets consisting on average of 4600 helium atoms. Comparison of the two spectra reveals that the signal in the high-mass range, corresponding to aniline ions solvated in helium droplets, is reduced in intensity when the ions are vibrationally excited. According to the standard thermal evaporation model, the mass spectrum should shift toward lower masses following the number of evaporated helium atoms. This is clearly not the case; only a reduction of the intensity is observed, but not a shift. This becomes even more evident when the ratio of the time-of-flight mass spectra with and without IR excitation is taken, see Figure 3B. One observes a constant signal reduction for masses larger than approximately 4000 amu, corresponding to ion-containing droplets consisting of more than 1000 helium atoms. In the mass range between 500 and 4000 amu, a somewhat smaller reduction is observed, while for masses below 500 amu, a strong enhancement of the ion signal is observed. The high-resolution spectrum in the low-mass range shown in the Figure 3C reveals that the signal enhancement in this mass range corresponds to the formation of bare aniline ions and small aniline$^+$−He$_n$ complexes. These observations are not specific to helium droplets of a particular size. As can be seen in Figure 3B, the same trends—that is, a constant signal reduction at high masses and a signal increase at low masses—are observed for a wide range of mean droplet sizes. These observations point directly to a mechanism in which aniline$^+$ and aniline$^+$−He$_n$ complexes are ejected from the droplets following IR excitation. Consequently, it appears that two processes contribute to the signal in the 500−4000 amu mass range in Figure 3B. First, the ejection of ions from small droplets in the distribution leads to a depletion of signal. Second, the formation of massive aniline$^+$−He$_n$ complexes, with n up to 1000, from the large droplets in the distribution gives rise to an increase of the signal. The overall effect of these two contributions appears as a small decrease. The fact that not only aniline$^+$ ions but also aniline$^+$−He$_n$ complexes are expelled from the droplets is probably the reason why, in Figure 2, the aniline ion yield is found to depend on the mean helium droplet size. While the ejection efficiency seems to remain constant, the ratio of bare aniline$^+$ to aniline$^+$−He$_n$ complexes most likely varies with droplet size.

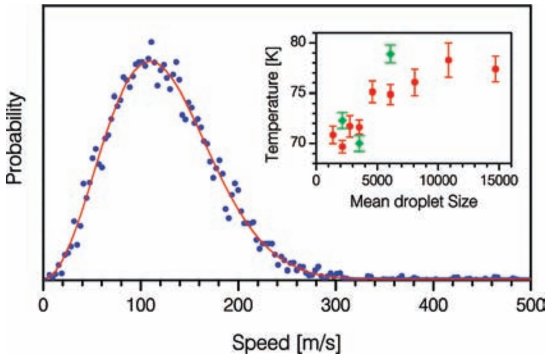

Figure 4. Speed distribution of aniline ions ejected from helium droplets consisting on average of 3500 helium atoms following excitation of the symmetric NH-stretch vibration of the aniline cation (blue dots). A fit of the data points to a Maxwell−Boltzmann distribution with a translational temperature of 72 K (red line). The inset shows the translational temperature of the aniline ions ejected from the droplets as a function of droplet size. The red dots correspond to excitation of the symmetric NH-stretch vibration at 3395 cm^{-1}, while the green diamonds correspond to excitation of the NH-stretch overtone at 6725 cm^{-1}.

Additional support for the ejection of the ions is provided by the speed distributions of aniline$^+$ and aniline$^+$−He$_n$ complexes. Figure 4 shows a typical speed distribution determined from the velocity map image of bare aniline ions following excitation of the NH-symmetric-stretch vibration of solvated aniline ions. This distribution, like all others, is well described by a Maxwell−Boltzmann distribution. The corresponding translational temperatures are found to depend weakly on the droplet size and range from 70 K for the smallest droplets to 78 K for the largest droplets used in this study. It should be noted that these temperatures are independent of the vibrational level that is excited. Excitation of the NH-stretch vibrational overtone, having almost twice the energy of the fundamental, does not result in a noticeable increase of the translational energy of the created ions. For the simple evaporation model, the translational temperature is expected to be comparable to the instantaneous temperature of the heated droplets, which can be readily estimated from the heat capacity of the droplets. We find that the observed temperatures are an order of magnitude higher than the expected temperatures. In addition, the droplet size dependence of the transitional temperatures is opposite to that expected on the basis of the heat capacities of the droplets.[52] Finally, the expected dependence of the ion translational

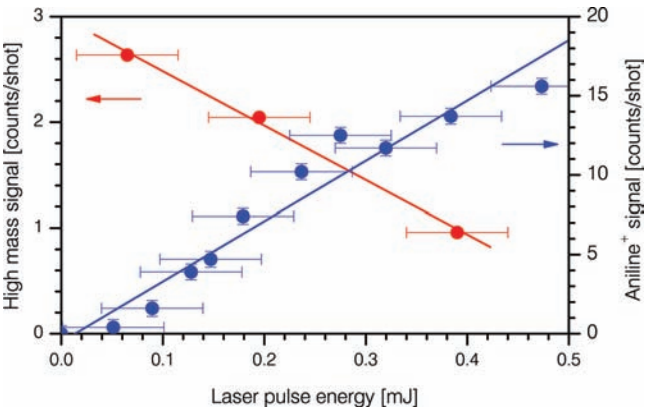

Figure 5. Signal levels of ion-doped helium droplets and of bare aniline ions as a function of pulse energy of the resonant IR radiation.

temperature on photon energy is not observed. Clearly, these results are not compatible with the simple evaporation model.

In order to rule out that the absorption of multiple photons is responsible for the ejection of the ions from the droplets, we have investigated the IR power dependence of the various results. As already mentioned above we found that the line shape of the transitions does not depend on the IR intensity. In addition, we also find that the speed distributions of the bare aniline ions and those of aniline$^+$$-He_n$ complexes do not depend on the IR laser intensity. This latter observation seems to indicate that the ejection of ions is indeed governed by a one-photon process. This is corroborated by the dependence of the signal levels on the IR intensity. Figure 5 shows, for droplets containing on average 8100 helium atoms, the integrated ion signal in the mass range of 4000$-$40 000 amu as a function of the pulse energy of the IR radiation resonant with the symmetric NH-stretch vibration. This signal decreases linearly with IR laser intensity, indicative that absorption of a single photon by the ions leads to their ejection. At the same time, the bare aniline ion signal, which is also plotted in Figure 5, appears to increase linearly with IR laser intensity within the present accuracy. These observations are all indicative of a one-photon process.

It is evident from the data presented above that vibrational excitation of ions in helium droplets leads to the expulsion of the ions by a nonthermal process. This result is quite opposite to what has been observed for neutrals, which have been found to cool by a thermal process after vibrational excitation.[63] However, the results are in line with the strong indications found in recent years that cooling of ions in helium droplets is governed by a nonthermal mechanism. As they use electron impact ionization, all these studies involve vibrationally hot ions. This makes it difficult to determine whether the nonthermal cooling is the result of ion solvation or vibrational excitation. The present study indicates that vibrational excitation of the ion plays an important role in the nonthermal cooling of ions. Whether solely the vibrational energy released into the droplet is responsible for the ejection of the ions cannot be determined from the data. For example, one could envision that a small barrier prevents the rearrangement of helium shells around the ion formed by photoionization of the neutral molecule. Vibrational excitation could help to overcome this barrier and release the rearrangement energy in addition to the vibrational energy. This scenario would be compatible with the fact that the kinetic temperature does not depend on the vibrational energy. However, the present data do not allow one to confirm or refute this possibility, nor do they allow one to determine the exact mechanism leading to the ejection of the ions. On the basis of the data, we can only propose a simple model that is compatible with our observations.

It is well established that ions, in contrast to neutrals, are surrounded by pronounced solvation shells due to the strong electrostatic interaction between an ion and helium.[24,45−47] We expect that, as a result, the vibrational energy of the ion will become localized within these solvation shells before being distributed over the whole droplet. This will give rise to a fast local heating of the helium environment and could lead to the formation of a local high-pressure gas bubble, as proposed first by Gspann[54] and later by Miller and co-workers.[57] This gas bubble could lead to the fission of the droplet or alternatively could expand until it bursts at the surface of the droplets and sets free the ion. Although the data presented here provide some glimpse into the mechanism for cooling ions in liquid helium, it is obvious that more studies, both theoretical and experimental, will be needed before the ejection mechanism can be definitively established.

4. Conclusion

We have recorded vibrational spectra of molecular ions in helium nanodroplets. The spectra are only very slightly shifted with respect to their gas-phase counterparts, which allows for the determination of the intrinsic properties of the ions. The widths of some of the transitions are significantly broader than the underlying rotational structure. This broadening has been attributed to the interaction of the ion with different helium solvation shells surrounding it. At the basis of the high sensitivity of the method is the nonthermal energy dissipation that leads to ejection of ions from the droplets. As a result, spectra can be recorded over a wide range of droplet sizes, making the technique very versatile. The method for ion production employed in the present study is intrinsically limited to a relatively small class of molecules. A much larger variety of systems can be investigated by doping helium droplets directly with ions.[25,26] In this way, it will become possible to investigate systems that may range from biomolecular ions such as polypeptides and proteins to ionic clusters. Our study opens up exciting new opportunities for the investigation of such ionic systems. For example, due to the greatly simplified spectra, it will become possible to map out the potential energy landscape of biomolecular ions, which is essential for understanding the conformational folding dynamics of these systems.[64] The opportunities are not limited to these particular types of systems. Now that a systematic spectroscopic investigation of atomic and molecular clusters of well-defined sizes at ultralow temperatures has come into reach, one can also envision exploring the onset of superconductivity in finite size systems.[65]

Acknowledgment. This work was supported by the Swiss National Science Foundation through Grant No 200020-119789 and The Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: Simulation of the rotational band contours. This material is available free of charge via the Internet at http://pubs.acs.org.

JA1034655

---

(63) Merritt, J. M.; Douberly, G. E.; Miller, R. E. *J. Chem. Phys.* **2004**, *121*, 1309.

(64) Dian, B. C.; Clarkson, J. R.; Zwier, T. S. *Science* **2004**, *303*, 1169.

(65) Ovchinnikov, Y. N.; Kresin, V. Z. *Eur. Phys. J. B* **2005**, *47*, 333.