Photoelectron Spectroscopy of Doped Helium Nanodroplets

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The photoionization dynamics of aniline doped helium droplets has been investigated by photoelectron spectroscopy. The photoelectron spectra resemble closely that of gas phase aniline, except for a droplet-size-dependent shift. This shift is caused by lowering of the ionization threshold upon solvation and can be readily estimated. The individual peaks in the photoelectron spectrum are broadened towards lower kinetic energy which is attributed to the relaxation of the photoelectrons as they pass through the helium droplet.

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During the last decade helium nanodroplets have been established as an ideal spectroscopic matrix [1]. Helium droplets are also thought to be ideal low temperature nanoreactors because of their ability to stabilize weakly bound species [2]. Since chemical reactions between neutrals generally have activation barriers that exceed by far the thermal energy of the dissolved reactants, attention is focusing onto ion-molecule reactions where such barriers are generally absent [3]. However, the spectroscopy and dynamics of molecular ions in helium has been much less well characterized than that of neutrals. A better understanding of these properties would certainly benefit future experiments on ion-molecule reactions. A powerful technique which is widely used in the gas phase to study ions is photoelectron spectroscopy. If applied to species residing in helium droplets, it could provide detailed information not only on stable molecules and their ions but also on weakly bound species that can be stabilized in helium droplets, e.g., reaction complexes [4]. In order to relate the observed photoelectron spectra to the electronic or vibrational structure of the ions it is important to have a detailed understanding of the photoionization dynamics in helium droplets. Although two studies have appeared in the literature on this subject, many questions still remain unanswered. In a first study pure helium droplets were ionized at a frequency just below the ionization threshold of atomic helium. The photoelectron spectrum was found to be dominated by slow electrons with energies in the meV range [5]. Even though the mechanism giving rise to the appearance of these slow electrons is still not fully understood, it is clear that relaxation of the photoelectrons plays an important role. In a more recent study Ag_8 clusters in helium droplets were investigated [6]. In contrast to the former study, the photoelectron spectrum is dominated by fast electrons. Assuming that the photoelectrons do not relax, the ionization potential of Ag_8 could be deduced from the spectra. This assumption seemed justified in view of the good agreement with the theoretical value of the ionization threshold, but at the same time appears to contradict the results of the earlier photoelectron study on pure droplets [5]. These two studies clearly show that if photoelectron spectroscopy is to be applied to helium droplets, a more detailed understanding of the photoionization dynamics is required. To address this issue, we have performed photoelectron spectroscopy on aniline both in gas phase and in helium droplets. Comparison of the spectra allows for a direct evaluation of the influence of the helium environment on the photoelectron spectra, thereby providing information on the photoionization dynamics in helium droplets.

The experiments are conducted in the following way. Helium droplets are formed by expanding high-purity ^{4}He gas at a pressure of 30 bars into vacuum through a 5 μm orifice cooled to cryogenic temperatures. The droplet size distribution can be systematically changed by variation of the source temperature [7]. The helium droplets pick up aniline molecules as they pass through a second vacuum chamber that is flooded with typically 10^{-6} mbar of aniline. The dissolved aniline molecules are subsequently resonantly ionized by the frequency doubled output of a Nd:YAG pumped dye laser system that crosses the droplet beam perpendicularly. The photoelectrons are accelerated towards a position sensitive detector by a set of electrodes that allow for velocity map imaging [8]. The detector is positioned some 40 cm away from the ionization region and consists of a microchannel plate assembly with phosphor screen. The light emitted by the phosphor screen is imaged onto a CCD camera interfaced to a PC. Using an inverse Abel transform, the kinetic energy distribution of the electrons can be determined from these images. To facilitate a direct comparison between gas phase and helium droplet spectra of aniline, the setup is equipped with an additional orifice that is kept at room temperature. A supersonic molecular beam containing aniline can be produced by expanding an aniline-argon mixture from this orifice.

As a first experiment, the resonance-enhanced multiphoton ionization (REMPI) spectrum of the $S_1 \leftarrow S_0$ transition in aniline is recorded by monitoring the total electron yield as a function of the laser frequency. The upper panel of Fig. 1 shows the spectrum of gas phase aniline. The spectrum shows a vibrational progression that has been analyzed previously [9]. The lower panel shows the excitation spectrum of aniline embedded in helium droplets. This spectrum is dominated by asymmetric broad features that follow to a large extent the gas phase spectrum. Closer inspection in the region of the band origin of the aniline spectrum reveals the presence of a weak sharp line (FWHM 1.1 cm^{-1}) which is located 35 cm^{-1} to the blue of the gas phase transition. Analogous to the spectra of other aromatic species dissolved in helium droplets, the sharp line can be interpreted as the zero-phonon line and the broad features as phonon wings. In contrast to other systems, for aniline the zero-phonon line is much weaker than the phonon wings. The saturation behavior of the observed features is also opposite to that observed for other aromatic systems. While for most systems studied up to now the intensity ratio of zero-phonon line to phonon wing decreases with increasing light intensity, this is not the case for aniline where the ratio increases with increasing light intensity; see the inset of Fig. 1. Both these observations on the relative intensities can be attributed to the large geometry change of the aniline molecule upon electronic excitation. Whereas aniline in the ground electronic state is nonplanar with the hydrogen atoms of the amine group pointing out of the aromatic plane, it becomes planar upon electronic excitation to the S_1 state [10]. The large geometry change of the aniline upon electronic relaxation requires a substantial reorganization of the helium environment around the molecule, which will give rise to an intense phonon wing and relative weak zero-phonon line [11].

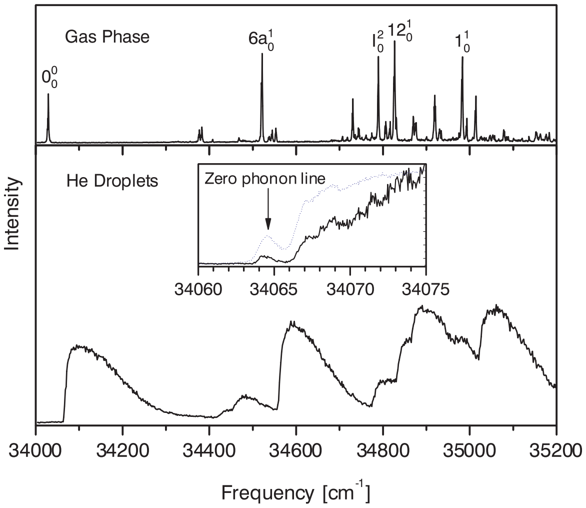

FIG. 1 (color online). $S_1 \leftarrow S_0$ excitation spectrum of aniline in the gas phase (upper panel) and in helium droplets (lower panel). The inset shows the weak zero-phonon line located to the red of the intense phonon wing corresponding to the band origin at low (solid line) and high (dotted line) light intensity, i.e., 7 $\mathrm{MW/cm^2}$ and 150 $\mathrm{GW/cm^2}$, respectively.

Photoelectron spectra are acquired by imaging the electrons onto the detector at a fixed frequency. The upper panel of Fig. 2 shows the photoelectron spectrum of gas phase aniline obtained by ionizing the molecules via the band origin of the $S_1 \leftarrow S_0$ transition. The spectrum shows several peaks that can be correlated to various vibrational levels in the ion [12]. The peak at the highest kinetic energy, corresponding to the vibrational ground state of the ion, can be used to determine the ionization potential of aniline. The value found, 62 304 cm^{-1}, agrees within its absolute uncertainty of 120 cm^{-1} to the literature value [13]. The lower panel of Fig. 2 shows the photoelectron spectra of aniline dissolved in helium droplets of two different sizes. These spectra are obtained by ionizing aniline via the maximum of the phonon wing corresponding to the band origin of the $S_1 \leftarrow S_0$ transition. The first point to note is that the onset of the photoelectron spectrum is shifted by about 800 cm^{-1} to higher energies with respect to the gas phase. Otherwise, the spectra resemble to a large extent that of gas phase aniline. However, there are some subtle differences. Upon closer inspection, the high kinetic energy peak appears to be asymmetrically broadened, especially for the larger droplets. There are also differences at low kinetic energy. The gas phase spectrum shows appreciable intensity at low kinetic energy and the same is true for small droplets. For the larger droplets these slow electrons are remarkably absent. We will now discuss these observations separately.

The shift of the photoelectron spectrum to higher energies can be attributed to a lowering of the aniline vertical ionization threshold in helium droplets with respect to the gas phase. In order to determine the actual shift of this threshold it is important to know whether relaxation of the helium excitations occurs on the time scale of the laser pulse. To address this issue and that of the relaxation of

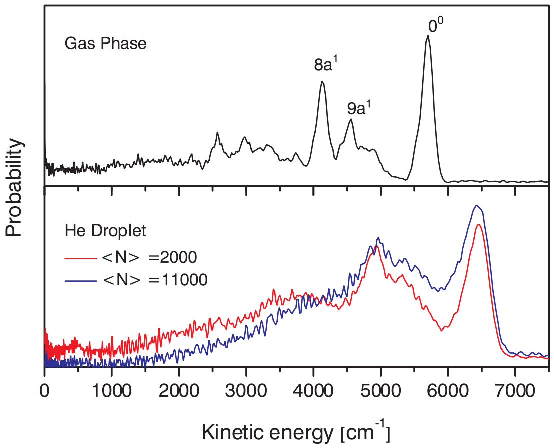

FIG. 2 (color online). Photoelectron spectrum of aniline in the gas phase (upper panel) and in helium droplets consisting on average of 2000 and 11 000 helium atoms (lower panel) recorded by resonance-enhanced multiphoton ionization via the band origin of the $S_1 \leftarrow S_0$ transition.

molecular vibrations, photoelectron spectra have been recorded at frequencies corresponding to the zero-phonon line, various positions in the phonon wing of the band origin, and various vibrational levels in the S_1 state. Figure 3 shows the position of the highest energy peak in the photoelectron spectrum as a function of the laser frequency. A linear fit of the data points shows that the photoelectron shift scales as the shift in laser frequency, implying that relaxation of the helium excitations as well as of the molecular vibrations occurs during the 5 ns laser pulse. Although the fit yields directly the energy difference between the ionization threshold and the level the system has relaxed to, it does not provide the absolute energy of this level. If one assumes complete relaxation of the helium and aniline excitations, then the energy of this level corresponds to the frequency of the zero-phonon line in the excitation spectrum. Making this assumption, the vertical ionization thresholds have been determined as function of droplet radius; see Fig. 4. Within the polarizable continuum model the vertical ionization threshold in clusters depends on the cluster radius R as:

$$\mathrm{IP}\,(R) = \mathrm{IP}_\infty - \frac{e^2(1-\varepsilon^{-1})}{8\pi\varepsilon_0 R}, \qquad (1)$$

where IP_∞ is the vertical ionization threshold in bulk helium, e the electron charge, ε_0 the permittivity of free space, and ε the dielectric constant of the cluster [14]. To determine the bulk vertical ionization threshold of aniline in helium, the observed thresholds have been fitted to the functional form of Eq. (1). The constant describing the R dependence is found to equal that given by the above equation, whereas the bulk ionization threshold is found to equal $\mathrm{IP}_\infty = 61\,470\ \mathrm{cm}^{-1}$, corresponding to a shift of $834\ \mathrm{cm}^{-1}$ with respect to the gas phase. This shift can also be assessed by theoretical methods. Using the Gaussian software package [15] the ionization thresholds of gas phase and dissolved aniline have been calculated within the framework of the polarizable continuum model. Since for aniline and its cation B3LYP (Becke three-parameter Lee-Yang-Parr) density functional calculations are found to yield more accurate results than *ab initio* calculations at the MP2 (second-order Møller-Plesset) level of theory [16], the calculations have been performed using the former method. In a first step the geometries of aniline and its cation were optimized using the $6\text{-}311++G(df,pd)$ basis set. The ionization threshold, given by the difference in energy between the neutral and cation at their optimized geometries, is calculated to equal $60\,815\ \mathrm{cm}^{-1}$, a value somewhat smaller than found experimentally. Subsequently, the energies in the presence of the helium solvent were calculated using the polarizable continuum model. Comparison of the ionization threshold found in these calculations to those without helium solvent gives a shift of $990\ \mathrm{cm}^{-1}$ for the ionization threshold, which is close to the experimental value. These results show that the observed ionization thresholds can be readily related to the gas phase ionization potential by taking into account polarization effects.

As already mentioned above, the peaks in the photoelectron spectrum are asymmetric; they show a droplet-size-dependent tail extending $100\text{–}300\ \mathrm{cm}^{-1}$ towards lower kinetic energies. Based on the rather small shifts of the ionization threshold with droplet size, it can be ruled out that this asymmetry reflects, via the droplet size dependence of the ionization threshold, the rather wide cluster size distribution [7]. As the ionization of the aniline results in a considerable rearrangement of the surrounding helium, broadening of the peaks in the photoelectron spectrum due to population of elementary excitations of the helium is not unlikely. This broadening is expected to be independent of droplet size and can therefore only be partially responsible for the observed peak shapes. Another contribution to the peak shape arises from the relaxation of the electrons as they pass through the helium liquid towards vacuum. Previous studies on the thermal-

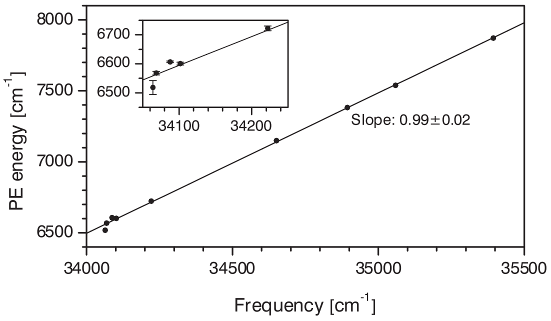

FIG. 3. Position of the highest energy peak in the photoelectron spectrum as a function of the laser frequency. The points at high frequencies correspond to excitations of molecular vibrations in the S_1 state of aniline. The points at low frequency are enlarged in the inset and correspond to excitation at the zero-phonon line and at different positions within the phonon wing of the band origin. The straight line is a fit to the data points.

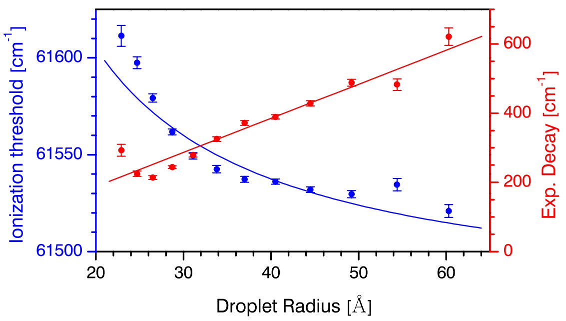

FIG. 4 (color online). Vertical ionization threshold of aniline in helium droplets as function of droplet radius (left axis). The solid line represents a fit of the data to Eq. (1). Variation of the exponential constant describing the asymmetric peak shape (see text) as function of droplet radius (right axis). The line is a linear fit to the data points.

ization of hot quasifree electrons indicate that the relaxation is mainly governed by elastic binary collisions between the electron and individual helium atoms [17,18]. At first, it might not seem likely that elastic collisions can be responsible for an energy loss in the order of 100 cm^{-1} in view of the small amount of energy transferred in these encounters, the modest collisional cross section [19], and the limited size of the droplets. However, if one considers the presence of the ion and the fact that the electron scattering is to a large extent in the backward direction [19] it is not unfeasible to have an energy loss of this magnitude. In order to address this possibility more quantitatively, the photoelectron peaks have been fitted to an empirical function that is a convolution of a Gaussian and exponential function. The Gaussian distribution is thought to represent the initial energy distribution of the electrons, whereas the exponential part is expected to reflect their relaxation. The widths of the Gaussian distributions are found to be 170 cm^{-1}, almost independent of droplet size. This width, which is 70 cm^{-1} larger than that in the gas phase, is believed to reflect the variation of the ionization potential with droplet size. The exponential decay constants shown in Fig. 4 are found to vary linearly as function of average droplet radius with a constant of $9.8 \pm 0.8\ \mathrm{cm}^{-1}\ \text{Å}^{-1}$. This linear dependence and the fact that the extrapolation of the curve to zero droplet radius goes through zero strongly suggests that the asymmetry of the peak shape is caused by the relaxation of the photoelectrons, rather than by population of elementary excitations of the helium environment. In order to determine whether this relaxation is due to elastic collisions, the relation between the relaxation efficiency and the electron energy has to be established. This is not possible in the current experiment but is feasible in a planned two color double-resonance experiment.

Closer inspection of the photoelectron spectra reveals that the appearance of low kinetic energy electrons is strongly droplet-size dependent. For all droplet sizes with radii smaller than 38 Å, photoelectrons down to zero kinetic energies are observed. For droplets larger than this radius photoelectrons with energies below $1230 \pm 50\ \mathrm{cm}^{-1}$ are absent. This energetic limit is found to be independent of droplet size. One can only speculate about the origin of this remarkable observation. Possibly it is caused by the localization of the slow electrons in the larger droplets followed by the recombination with the positive aniline ion. A more detailed discussion of these observations will be given in a future publication.

In conclusion, we have shown that photoelectron spectroscopy can be successfully applied to molecules dissolved in liquid helium droplets. The photoelectron spectra of dissolved aniline resemble closely that of gas phase aniline, except for a droplet-size-dependent shift. This shift is related to the lowering of the ionization threshold due to polarization effects and can be readily estimated. The individual peaks in the photoelectron spectrum are broadened towards lower kinetic energy, which can be attributed to the relaxation of the photoelectrons. The absence of slow electrons for droplets larger than a critical radius is tentatively ascribed to the localization of the electrons. The current work shows that the relaxation of the photoelectrons depends on droplet size and possibly electron energy and thereby reconciles the apparent discrepancy between the two previous studies [5,6] on photoelectron spectroscopy on helium droplets.

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