

Electron delocalization by polar molecules: Interaction of Na atoms with solid ammonia films studied with MIES and density functional theory

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The interaction of Na and NH₃ on tungsten was studied with metastable impact electron spectroscopy under UHV conditions. NH₃(Na) films were grown at 90(±10) K on tungsten substrates and exposed to Na(NH₃). No Na-induced reaction involving NH₃ takes place. At small Na exposures a Na-induced shift of the NH₃ spectral features is seen, in parallel with a decrease of the surface work function. At larger exposures three 3sNa-related spectral structures are seen, two of them at energetic positions different from that found for Na on metals or semiconductors. The main additional peak is attributed to delocalized Na species. A small additional feature is attributed to simultaneous ionization and excitation of partially ammoniated Na₂ species. The results are compared with density functional theory calculations which suggest that the 3sNa emission at small exposures appears to originate mainly from delocalized 3sNa electrons; they are located far from the Na species and become stabilized by solvent molecules. When depositing NH₃ molecules onto Na films, metalliclike Na patches and delocalized Na species coexist. The delocalization of 3sNa is seen up to $T=130$ K where the NH₃ species desorb. © 2004 American Institute of Physics. [DOI: 10.1063/1.1772751]

I. INTRODUCTION

Electron solvation during the interaction of Na with liquid ammonia is well established. However, despite many efforts, the structure and the localization mode of the solvated electrons is still subject of intense discussions. One particular reason is that it is not easy to obtain direct detailed information on the 3sNa electron which plays an active role in this process. Recently, the study of solvated electrons in finite clusters has furnished information on the microscopic aspects of the solvated states. Neutral and negatively charged hydrated and ammoniated Na clusters were prepared by the capture of low-energy electrons. The properties of ammoniated Na monomer and dimer clusters have been studied, as a function of cluster size, by photoelectron, photoion, and related spectroscopies as well as by first-principles density functional theory (DFT).¹⁻⁵

Another promising approach appears to be the study of the interaction of Na species with solid molecular films.^{6,7} Previously, we have studied the interaction of Na with films of solid water and methanol by combining metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS).⁶⁻¹² As compared to UPS, MIES possesses a rather large sensitivity for the detection of the 3sNa electron, and its pronounced surface sensitivity allows, in

combination with UPS, to distinguish between species adsorbed atop and underneath the surface under study. These studies concentrated on the role played by the 3sNa electron for the Na-induced water dissociation and methoxy formation. First-principles DFT calculations on Na-water clusters suggest that the 3sNa electron becomes delocalized from its Na⁺ core and is trapped between the Na⁺ (and eventually Na₂⁺) species and surrounding water molecules.¹³ A peculiar structure seen in the MIES spectra near the Fermi level appears to be characteristic for delocalized 3sNa electrons.^{7,11} The extension of this work to Na-ammonia and methanol clusters¹⁴ indicated that the delocalized electrons play a key role in the deprotonation of water and methanol.

In the present paper we apply MIES to the study of the interaction of Na and ammonia on a cold tungsten substrate. By combining the experimental results with the above-mentioned DFT calculations,¹⁴ we conclude that the 3sNa electrons become delocalized. The combined results from theory and experiment shed light onto the underlying mechanism for this process. It is suggested that Na₂ dimers are involved in the solvation process.

II. THEORETICAL DETAILS AND RESULTS

The method of computation was fully exposed and applied to the solvation of the sodium atom by water in Refs. 13 and 14. The solvation of Na by ammonia and methanol has been studied by an analogous strategy and compared with hydration.¹⁴ Briefly, DFT calculations were carried out at the B3LYP/6-31+G(*d,p*) level of approximation. This

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was performed on several cluster models in order to investigate the potential energy surfaces associated to neutral sodium ionization by solvation. Two models were considered: solvation of a single sodium atom or of a sodium dimer. In both cases we tried to embed the sodium into the solvent cluster as completely as possible. The DFT functional, the orbital basis set and all the computational ingredients can be found in Ref. 13.

It was established by the comparison of the MIES with UPS spectra that the interaction of He^* with clean and Na covered ammonia films is via the Auger deexcitation process.⁶ This implies that the MIES spectra image the surface density of states (SDOS) directly.^{15,16} The SDOS, needed for the comparison with the MIES spectra, have been obtained by dressing the DFT molecular energy level distributions with Lorentzian functions of arbitrary height and a half width of 0.25 eV.

In the case of monomer solvation, a $\text{Na}(\text{NH}_3)_6$ cluster was treated [see Fig. 1(a) of Ref. 14]. The ammonia molecules organize themselves in two layers:

(i) In the first layer, the nitrogen atoms are located at nearly equal distances from Na (between 2.464 and 2.539 Å). All the N-H bonds point toward the outside of the cluster and no hydrogen bond is established between the solvent molecules.

(ii) The sixth ammonia has been introduced in the model in an attempt to surround the Na atom more completely. This “extra” molecule bonds to the first solvent layer by a hydrogen bond.

For $\text{Na}_2(\text{NH}_3)_{11}$ the metal dimer was embedded, as completely as possible, into the solvent cluster [see Fig. 1(b) of Ref. 14]. Eleven NH_3 solvent molecules were required for this purpose. The whole system consists of two subsystems, each one centered in the vicinity of the two alkali atoms found at a distance of 3.95 Å from each other. In the larger subsystem, the Na is at distances of about 2.5 Å from its closer NH_3 neighbors. This ensemble is surrounded by a second shell of NH_3 molecules that interact via H bonds. The other Na is bonded to a single ammonia. As in the hydration case, a tendency is found for the second alkali to remain at the “surface” of the cluster.

The DOS from the cluster DFT calculations for a pure $(\text{NH}_3)_{10}$ cluster and the solvated cases $\text{Na}(\text{NH}_3)_6$ and $\text{Na}_2(\text{NH}_3)_{11}$ will be compared with the MIES spectra for Na adsorbed on NH_3 films (Fig. 4).

III. EXPERIMENTAL DETAILS AND RESULTS

The apparatus and the experimental procedures are described in detail elsewhere.^{11,17,18} The electronic structure of the molecular films produced on a tungsten substrate was studied by applying MIES and UPS (He I and II). In MIES metastable helium atoms ($2^3S/2^1S$) eject electrons from the edge of the surface under study. The application of MIES to surface spectroscopy, and its combination with UPS (He I and II) is well documented.^{15,16}

The primary result of the experiments are energy spectra of the emitted electrons versus their kinetic energy. By choosing a suitable bias voltage between the target and the electron energy analyzer, the energy scales in the figures are

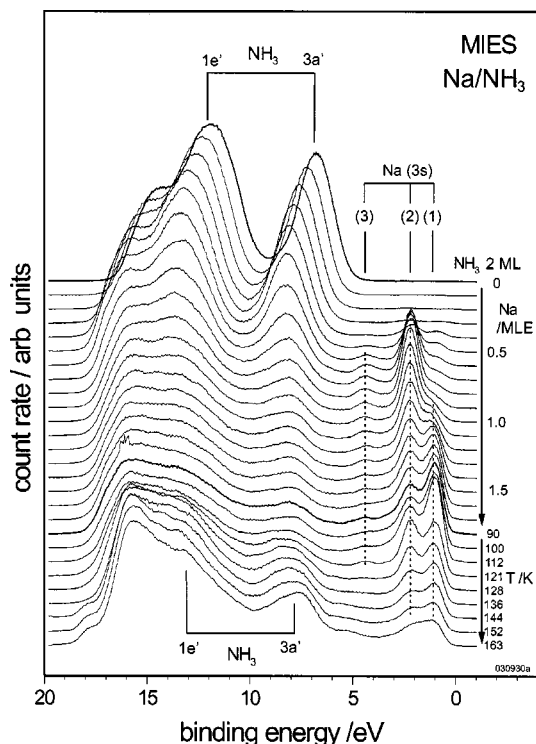


FIG. 1. MIES spectra for the adsorption of Na on solid NH_3 (two layers) prepared on tungsten (90 K) (upper set of spectra), and the spectral changes resulting from annealing in the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

adjusted in such a way that electrons emitted from the Fermi level, denoted by E_F , i.e., electrons with the maximal kinetic energy, appear at 19.8 eV (which is the potential energy of the metastable He atoms employed for MIES). With this particular choice of the bias voltage, the low-energy cutoff in the spectra gives directly the surface work function (WF), irrespective of the actual interaction process which produces the electrons. For a convenient comparison with theory we present our data as a function of the binding energy of the emitted electrons prior to their ejection. Electrons emitted from the Fermi level, i.e., those with the 19.8 eV kinetic energy, appear at binding energy $E_B=0$ eV with respect to the Fermi level. The surface temperature can be varied between about 90 and 700 K; at present the accuracy of the temperature calibration is 10 K. The surface was exposed to NH_3 by backfilling the chamber at a substrate temperature of 90 K. The Na exposure is given in units of monolayer equivalents (MLE); at 1 MLE the surface would be covered by one Na monolayer if penetration of the Na into the molecular films could be neglected. The amount of surface-adsorbed ammonia can be estimated from the variation of the tungsten substrate intensity at the Fermi edge in the UPS (He I and II) spectra.

If the Na adsorbate is not fully ionized, a strong spectral feature from the presence of 3s-charge density at the Na core is seen with MIES, but not UPS. For the study of the Na-induced changes in the electronic structure of the molecular films we have therefore confined ourselves in reporting the MIES results.

Figure 1 presents MIES results for the interaction of Na

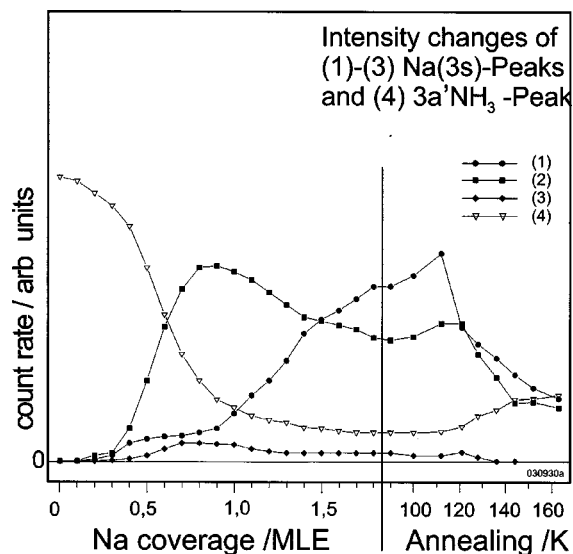


FIG. 2. Intensities of the Na-induced peaks (1) to (3) (localized and solvated $3s\text{Na}$, and the satellite of (2), respectively) and of $3a'\text{NH}_3$ (4) vs the Na exposure and during the heating of the Na/ NH_3 system (data from Fig. 1).

with a NH_3 film held at 90 K. The top spectrum is for the ammonia film (two layers thick) prior to Na exposure. The upper set of spectra is obtained during the Na exposure. The lower set of spectra displays the spectral changes observed during film annealing in the indicated temperature range. According to Ref. 19 the two broad features observed at $E_B = 6.5$; 11.3 eV in the MIES spectra of the ammonia film are due to the ionization of the $3a'$ (n_N) and $1e'$ [$\pi(\text{NH}_2)$], respectively. A shift of these features takes place, correlated with the Na-induced decrease of WF. With increasing Na exposure three Na-induced structures (1)–(3) appear, located at 1.3, 2.3, and 4.5 eV with respect to the Fermi level ($E_B = 0$ eV). At low exposures we attribute (1), by comparison with the corresponding feature for Na adsorption on metals and semiconductors, to $3s\text{Na}$ ionization from neutral isolated Na atoms; at larger exposures (1) comes from patches with metalliclike properties. By comparison with the interaction of Na with water and methanol ices,^{7,10,11} we attribute (2) (at 2.3 eV) to delocalized electrons (see Fig. 4 for a comparison with theory). When heating from 90 to 163 K $3a'\text{NH}_3$, (2) and (3), but not (1), pass through maxima around 120 K, and finally decay with temperature (for details see Fig. 2). According to MIES, NH_3 has practically sublimated from bare tungsten at 130 K, it is obvious from Fig. 1 that, due to its interaction with Na, sublimation is delayed by at least 30 K.

Figure 2 displays the exposure dependence of the intensities of the Na-induced peaks (1)–(3), seen between $E_B = 0$ and 5 eV, and of $3a'\text{NH}_3$ [curve (4)] (data from Fig. 1). Peaks (1)–(3) become sizable around 0.3 MLE whereby (2) and (3) display a similar exposure dependence, suggesting that the emission has a common origin. In the following (3) is considered as a satellite of (2) (see Sec. IV). A clear correlation appears to exist between the three Na-induced signals and $3a'\text{NH}_3$ [peak (4)]: when (2) saturates, (4) has essentially decayed. On the other hand, (1) rises after (2) and (3) have leveled off, and (4) has decayed. Also included is the change of the signals' intensities upon heating. All Na-

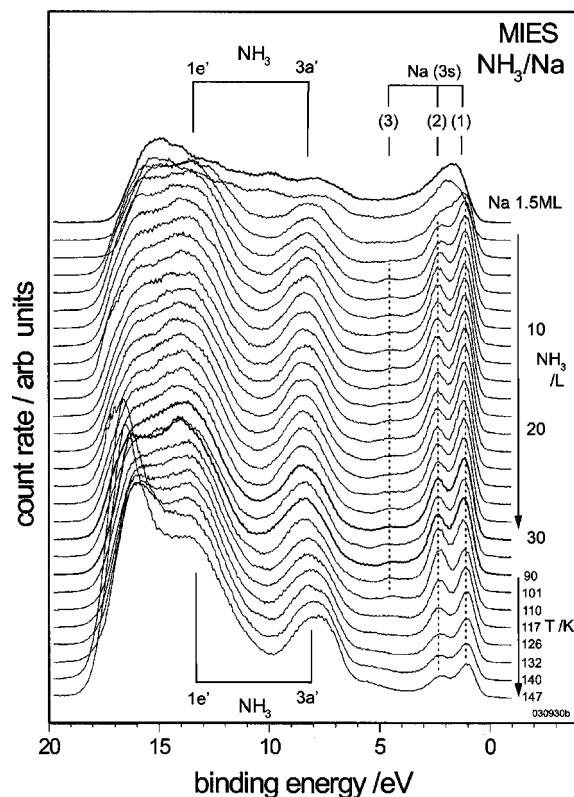


FIG. 3. MIES spectra for the Na film (1.5 layers prepared on tungsten (90 K) (upper set of spectra) exposed to NH_3 molecules, and the spectral changes resulting from annealing over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

induced signals display a sharp break around 120 K, close to the temperature where thermal desorption of ammonia films takes place (125 K).²⁰

Figure 3 presents MIES results for NH_3 molecules interacting with a Na film held at 90 K. The top spectrum is for the Na film (saturation coverage at 90 K; 1.5 ML) prior to NH_3 exposure. The upper set of spectra is for NH_3 exposure at 90 K. The lower set of spectra displays the spectral changes observed during film annealing in the indicated temperature range. As a consequence of the exposure, the NH_3 structures $3a'$ and $1e'$ appear at $E_B = 7.8$ and 13.2 eV, respectively. Initially, the $3s\text{Na}$ electron in metallic environment manifests itself by the comparatively broad structure just below E_F which is known to be due to the Auger deexcitation process involving the $3s\text{Na}$ electrons. Following ammonia exposure, a peak appears at 1.3 eV which, as for the clean Na film, is due to the interaction of the He^* probe atom with the $3s\text{Na}$ electron; however, because the surface work function has reduced 0.5 eV to below 2 eV, it is now mainly due to autodetachment of He^{-*} temporary negative ions formed by the resonant capture of a $3s$ electron by the probe atom.^{15,16} Peak (2) (2.3 eV), appearing together with its satellite (3), is again attributed to ammoniated Na; the structures attributed to the delocalized species weaken as a consequence of film annealing.

IV. INTERPRETATION AND DISCUSSION

Figure 4 summarizes the computational and experimental results by comparing the DOS of the cluster DFT calcu-

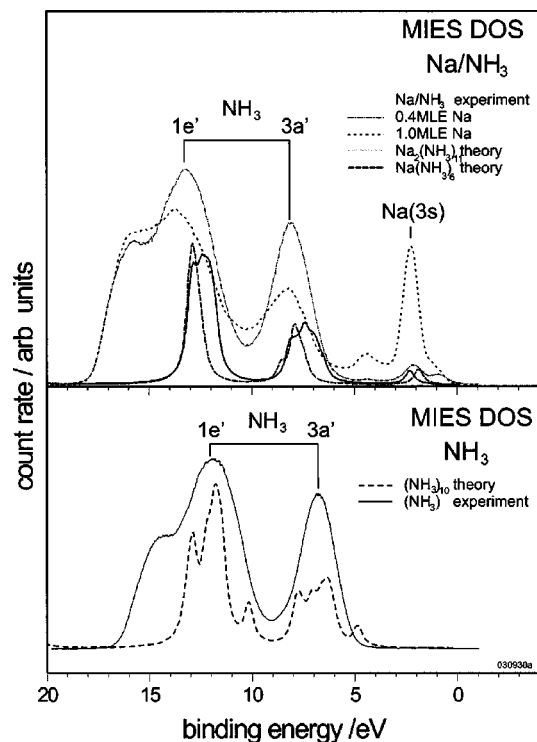


FIG. 4. Comparison of the DOS results for various clusters with selected MIES spectra (Fig. 2). Bottom: bare NH_3 film and $(\text{NH}_3)_{10}$ cluster. Top: Na/NH_3 and the clusters $\text{Na}(\text{NH}_3)_6$ and $\text{Na}_2(\text{NH}_3)_{11}$.

lations and the MIES spectra. For pure NH_3 the DOS displays the structures from the $1e'$ and $3a'$ derived states in the energy range accessible to MIES; in the solvated cases also the contribution, originating from the delocalized $3s$ Na electron, is seen. General agreement with experiment exists in the positions of the observed main features, namely, those from the ionization of the NH_3 MOs and the peak (2), attributed to $3s$ Na delocalization (2.3 eV). Peak (1), attributed to emission from $3s$ electrons localized at the Na core, is not reproduced by the chosen model. The calculations do also not reproduce structure (3) centered around 4.5 eV. The good general agreement noticed otherwise between theory and experiment suggests that (3) may not be a feature of the DOS of the system (see below). The inspection of the results without and with Na confirms that, as under liquid conditions, no Na-induced reaction takes place. Theory correctly predicts, but underestimates the shift of $3a'$ and $1e'$ of NH_3 towards larger binding energies as a consequence of the Na adsorption. The agreement in the position of the Na-derived peak (2), with respect to the valence band maximum, for both the Na monomer and dimer cases provides evidence for the presence of delocalized $3s$ Na electrons at the film surface. However, the presence of peak (2) does not necessarily imply that the Na species are fully solvated; there is ample evidence that $3s$ Na delocalization takes already place when Na interacts with a single NH_3 molecule.^{1–5} After a Na exposure of 1.5 MLE a rather dense Na layer is obtained on top of the ammonia film as judged from the decay of the $3a'$ NH_3 signal. The large intensity of (2) suggests that strong interaction exists between Na and NH_3 in the toplayer. We tend to believe that Na, does not become fully solvated as a conse-

quence of the annealing because (2) remains strong up to 160 K where part of the NH_3 has already desorbed. On the other hand, it cannot be excluded that some $3s$ Na charge density “leaks through” an eventual solvation shell, and, thus, becomes accessible to MIES.²¹

Peak (3), the satellite of (2), deserves some additional considerations. In order to arrive at a convincing explanation for its origin, we anticipate that partially ammoniated Na_2 species are produced during the Na exposure onto the solid ammonia film. This may happen quite naturally by attaching an additional Na atom to an existing $\text{Na}(\text{NH}_3)_n$ cluster. The interaction of Na atoms with hydrated Na clusters was studied previously by inserting a neutral Na atom next to $\text{Na}(\text{H}_2\text{O})_n$ ($n=6,8$).²² Wave function minimization leads to the formation of a so-called dipolar sodium anion: the negative charge in the highest occupied molecular orbital becomes localized between the two Na atoms, close to, but not coinciding with the core of the unsolvated one, hence giving it its dipolar character. We suppose that the Na interaction with $\text{Na}(\text{NH}_3)_n$ takes place in a similar way as for the hydrated case, and leads to ammoniated $\text{Na}_2(\text{NH}_3)_{11}$ complexes whose charge distribution is similar as in Fig. 2(b) of Ref. 14. As for hydration, a clear tendency of the second Na to remain at the surface of the ammoniated cluster can be anticipated. In order to explain the occurrence of the satellite, we assume that simultaneous excitation and ionization of the ammoniated Na_2 takes place in MIES during its ionization in the Auger deexcitation process. Hereby, a transition takes place to excited states of the ammoniated Na_2^+ system during the ionization process. This process sequence was studied for ammoniated Na_2^- anions by combining first-principles calculations with photoelectron spectroscopy.¹ Spectral contributions are seen which correspond to transitions from the ground state of ammoniated Na_2^- to excited states of ammoniated neutral Na_2 , i.e., to electron detachment accompanied by excitation of the cluster. The $3s$ solvation leads to large redshifts of the energies for the transitions from the anionic ground state to excited states correlating with $[\text{Na}(^2S) + \text{Na}(^2P)]$. It appears not unreasonable to expect that, as in the case of simultaneous ionization and excitation of the ammoniated anion,¹ the spectral features from simultaneous excitation and ionization of the Na_2 ground state to excited states of Na_2^+ are located about 1.5–2.5 eV above the peak attributed to the Na_2 ground state. Thus, the comparison with the photoelectron spectra for solvated Na_2^- (Ref. 1) gives confidence that peak (3) is due to processes involving (partially) ammoniated Na_2 species. Consequently, the existence of the satellite can be considered as evidence that ammoniated dimers are formed during the Na interaction with solid NH_3 films.

Finally, the interaction of NH_3 molecules with the Na adlayer will be discussed (Fig. 3). Even after an exposure of 30 l NH_3 the Na film is not entirely covered by NH_3 . As was discussed above, some $3s$ Na charge density may be seen through a NH_3 adlayer. However, it appears safe to conclude, on the basis of the strong $\text{Na}(3s)$ signal seen at all temperatures, that no NH_3 multilayers are formed at 90 K on top of the Na film. Upon annealing (2) becomes more pronounced relative to (1) before it fades away with the onset of NH_3

desorption, suggesting that a temperature-induced rearrangement takes place within the Na-NH₃ system.

V. CONCLUSIONS

The present study, combining metastable impact electron spectroscopy (MIES) with DFT calculations, is devoted to the Na interaction with ammonia ice. It concentrates on the role played by the Na3s electron in the interaction process. The MIES spectra from pure ammonia ice at 90 K are in good agreement with the DFT cluster density of the states of NH₃. Two models for the Na-ammonia interaction were considered, solvation of a single Na atom and of Na dimers. Theory and experiment agree that no Na-induced reaction takes place. The agreement of the MIES spectra with the predictions of both solvation models is rather satisfactory, in particular, concerning the ionization energy of the 3s electron in the NH₃ environment. This suggests that MIES detects 3s electrons, delocalized from their Na⁺ core and trapped between the core and surrounding solvent molecules; this reduces the ionization energy by about 1 eV as compared to isolated Na species. A satellite, correlated with the main peak from delocalized 3sNa, is seen in the experiment. We attribute it to the simultaneous excitation and ionization of delocalized electrons in Na dimers during their interaction with the He* probe atoms in MIES. This provides evidence that dimers play a role in the Na-NH₃ interaction.

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