Thermal and Photodesorption from a Molecular Surface: Ammonia on Ag_2

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The one-to-one complex Ag_2NH_3 was prepared by titrating disilver with ammonia. Its photodissociation along ground and excited state potential surfaces was studied. Binding energies and the ammonia umbrella frequency were determined to be in good accord with precise electronic structure calculations showing that the complex is linear. Complexes of this type are important members of a series that extend to infinite surfaces. They allow the dynamics of particular adsorbate excitations to be isolated. Here, an excitation at 3 eV involving the metal-metal *and* the chemisorption bond is revealed.

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Following Smalley's introduction of the laser ablation source for beams of metal clusters [1], the *molecular surface science* approach to adsorbate interactions with metal centers was recognized [2]. This approach parallels the *cluster-surface analogy* of Mutterties *et al.* [3] but with the advantage that the high degree of unsaturation, typical of bare metal surfaces, is mimicked.

The study of single crystal surfaces in ultrahigh vacuum provides another approach, with a long and glorious history, particularly amenable to the study of the long-range and cooperative effects which are important on extended surfaces. Singly ligated metal clusters will provide a series of models, extending to infinite surfaces, and emphasizing short-range interactions. One-to-one association complexes involving ligands and metal dimers are important members of this series, as their structure and dynamics can be discussed in purely molecular terms and particular adsorbate excitations can be isolated. In this Letter we report the first experimental study of such a complex, Ag_2NH_3.

We studied photodissociation of the complex along ground and excited state potential surfaces, together with electronic and vibrational spectra. These reveal details of the chemisorption bond. High level calculations using density functional theory are in excellent agreement with the experimental results and show the complex to be linear. A simple molecular orbital description gives an understanding of the results at an intuitive level. A particular adsorbate excitation, involving the chemisorption bond, is found at 3 eV and it dynamics is reported.

Cluster structure and photodepletion spectroscopies.— There are two notable problems in *molecular surface science*. The first is the structure of the metal clusters [4–7]. Only a few clusters have been studied spectroscopically, most notably Si_6 [4], and photodepletion techniques have proven advantageous [6,7]. For others, ligand-uptake measurements give a chemical probe of the structure [8]. Density functional (DFT) and other *ab initio* theoretical methods are capable of accurate calculations on clusters of significant size [9].

The second challenge is to characterize the cluster-ligand interaction. The IR spectra of weakly bound ligands can be measured using infrared multiple photon dissociation (IRMPD). In molecules with a sufficient density of vibrational states, resonant absorption of the first few photons is the rate-determining step [10], and the IRMPD action spectrum is linked to the small-signal IR absorption spectrum. Zakin *et al.* obtained an IR spectrum for methanol adsorbed on iron clusters in this manner [11].

Preparation of complexes.—This Letter is based on a study of the reactivity of coinage metal dimers using a large bore, He-buffered flow reactor into which metal clusters are injected from a laser ablation source [12–14]. The reactor has a pressure range of 0.4 to 9 Torr and uses laser induced fluorescence (LIF) to monitor metal cluster concentrations downstream from a reagent inlet [13,14]. For Ag_2 reacting with ammonia in the gas phase at room temperature, we showed that an equilibrium amount of an association complex is formed

$$Ag_2 + NH_3 \rightleftharpoons Ag_2NH_3 . \qquad (1)$$

We have also shown that Ag_2NH_3 does not go on to add a second NH_3 ligand on the time scale of the experiment. Using the measured equilibrium constant [$K_p = (4.6 \pm 0.3) \times 10^{-15}$ cm^3 at 297 K] [12] we are able to set up reactor conditions such that all Ag_2 is converted into Ag_2NH_3.

A simple molecular orbital (MO) picture for the NH_3-Ag_2 bond.—An MO treatment for Ag_2NH_3 shows that the side-on approach will be destabilizing due to the Pauli repulsion between the σ orbital and the ammonia lone pair. For the end-on approach, however, there is a strong interaction between the empty σ^* (acceptor) orbital on Ag_2 and the n (donor) orbital of NH_3. Net bonding is obtained as the stabilization of the $n(NH_3)$ orbital more than counteracts the destabilization of the $\sigma(Ag_2)$ orbital. The mixing of the σ and σ^* orbitals, caused by the ligand-induced symmetry breaking, allows polarization to alleviate repulsion between the σ electrons and the lone pair. In the ground state of the complex, the four electrons occupy the two lower MO's [$n(\mathrm{NH}_3)$ and $\sigma(\mathrm{Ag}_2)$]. The lowest unoccupied molecular orbital $\sigma^*(\mathrm{Ag}_2)$ will be more destabilized than the $\sigma(\mathrm{Ag}_2)$ orbital. Thus the photodissociation excitation spectrum of $\mathrm{Ag}_2\mathrm{NH}_3$ is blueshifted with respect to the A-X transition of Ag_2, and the excited state is dissociative along the silver-nitrogen bond.

Density functional calculations of the structure and properties of Ag_2NH_3.—The qualitative picture presented is confirmed by high level electronic structure calculations carried our using the linear combination of Gaussian-type orbitals density functional method [15], as implemented in the program DEMON [16]. The local spin-density potential of Vosko, Wilk, and Nusair (VWN) was used in the self-consistent (SCF) solution of the Kohn-Sham equations [17]. The calculation of the forces, equilibrium geometries, and vibrational frequencies was done at the VWN level. Gradient corrections were added non-self-consistently to the exchange [18] and correlation [19] terms of the total energy. The scalar relativistic model core potential (MCP) of Andzelm, Radizo, and Salahub was used to represent the $1s^22s^22p^63s^23p^63d^{10}4s^2$ closed shells of Ag [20]. The Kohn-Sham orbitals were expanded using the $6s$-$5p$-$4d$ basis with contraction pattern (2211-2111-121) for Ag [20], the 6-31 + G^* Gaussian basis with pattern (6311-311-1) for N [21], and a basis with pattern (311-1) for H. The auxiliary basis sets for fitting the charge density and those for fitting the exchange correlation potential have the same form. They are uncontracted and the smallest exponents are shared by functions of s, p, and d type. On Ag the auxiliary bases consisted of ten s, seven p, and seven d functions, on N they had the form (8,4,4), and for H the bases were of the type (6,2,2). Geometry optimization was carried out with a standard gradient method. Harmonic vibrational analysis was performed through finite differences of analytical gradients.

Ground state $\mathrm{Ag}_2\mathrm{NH}_3$ was found to have the linear, end-on, C_{3v} structure. No other stable geometries were found. The binding energy E_0 was calculated as 12.3 kcal mol^{-1}, the Ag-Ag bond length as 2.49 Å, and the Ag-N bond length as 2.19 Å. Full details of the vibrational analysis will be reported separately [22]. The harmonic frequency of the NH_3 umbrella mode of the complex was calculated to be 1102 cm^{-1}, 153 cm^{-1} larger than calculated for free NH_3 (949 cm^{-1}).

Measured binding energy for Ag_2NH_3.—The equilibrium constant suggests $E_0 = 14.7 \pm 2$ kcal mol^{-1} from third-law modeling studies using the structure and vibrational frequencies predicted by the DFT calculations. From the temperature dependence of the equilibrium constant we find a value for ΔH_{307° of 16.4 ± 3 kcal mol^{-1}, from which we obtain $E_0 = 15.9 \pm 3$ kcal mol^{-1} [23].

UV photodissociation of Ag_2NH_3.—Excitation of the $\mathrm{Ag}_2\mathrm{NH}_3$ complex at ~310 nm, using an excimer laser-pumped dye laser, results in the emission of light, identified as the $A \rightarrow X$ transition of the silver dimer Ag_2. The excitation spectrum peaks at 308 nm with a FWHM of ~30 nm. Proof that this signal is indeed associated with Ag_2 ($A\,^1\Sigma_u$) coming from the UV photodissociation of $\mathrm{Ag}_2\mathrm{NH}_3$ is found in experiments linking the $A \rightarrow X$ emission intensity to the concentration of $\mathrm{Ag}_2\mathrm{NH}_3$ in the flow, as determined by $p(\mathrm{NH}_3)$, the pressure of NH_3. As required, the reciprocal of the emission intensity is linear with respect to $1/p(\mathrm{NH}_3)$, yielding an equilibrium constant identical to the one reported for reaction (1). The emission spectrum, peaking at 445 nm, and the fluorescence lifetime, 6.3 ns, identify the transition by comparison to the known spectroscopy of Ag_2 [5]. Modeling the emission spectrum indicates that Ag_2 ($A\,^1\Sigma_u$) is produced with a vibrational temperature of ~600 K.

A simple picture of the photodissociation dynamics emerges from these results. A UV photon populates a σ^* state in which there is now Pauli repulsion of the filled $n(\mathrm{NH}_3)$ orbital. This state correlates to Ag_2 ($A\,^1\Sigma_u$). At 308 nm there is an excess energy of 13 kcal mol^{-1} ($D_0[\mathrm{Ag}_2\mathrm{NH}_3(X)] = 14$ kcal mol^{-1} [12,14], $T_0[\mathrm{Ag}_2(A\,^1\Sigma_u)] = 66$ kcal mol^{-1} [5]). The vibrational excitation of Ag_2 ($A\,^1\Sigma_u$) is consistent with an end-on structure and a disscociative excited state. Conservation of energy and momentum in a limiting impulsive model predicts a vibrational temperature of 710 ± 56 K in Ag_2 ($A\,^1\Sigma_u$). Experimentally we find ~600 ± 100 K which could suggest the involvement of bending vibrations of the complex. A more detailed discussion of the photodisscociation dynamics of $\mathrm{Ag}_2\mathrm{NH}_3$, and $\mathrm{Cu}_2\mathrm{NH}_3$, which shows similar but more complicated behavior, will be given elsewhere [23].

IR photodissociation of Ag_2NH_3.—The experiments on UV photodissocaition of $\mathrm{Ag}_2\mathrm{NH}_3$ suggest two methods to measure IRMPD action spectra. Following the IR laser pulse with an overlapping UV pulse from the dye laser at ~308 nm, at a time delay short enough to avoid mass transport losses, produces an emission signal that probes the amount of $\mathrm{Ag}_2\mathrm{NH}_3$ left after IRMPD. Alternatively, following it with a laser tuned to an Ag_2 resonance, after a time delay sufficient to allow for relaxation of the nascent Ag_2 ($A\,^1\Sigma_u$), produces a signal proportional to the amount of IR-photodissocaited $\mathrm{Ag}_2\mathrm{NH}_3$.

We carried out both of the above experiments using a line-tunable, pulsed, CO_2 laser, see Fig. 1. Note that the spectrum for $\mathrm{Ag}_2\mathrm{NH}_3$ depletion is matched by that for production of Ag_2. Excitation in other CO_2 laser bands (923–956 and 965–988 cm^{-1}) showed no evidence for IRMPD. We suggest that the IRMPD is enhanced by a resonance with the umbrella mode of the $\mathrm{Ag}_2\mathrm{NH}_3$ complex and that its frequency is 1065 ± 5 cm^{-1}. We see no IRMPD of $\mathrm{Ag}_2\mathrm{NH}_3$, whose umbrella frequency is ~200 cm^{-1} lower. It is an accident of nature that the peak in the IRMPD of $\mathrm{Ag}_2\mathrm{NH}_3$ lies in the inaccessible region between 1060 and 1068 cm^{-1}. However, the resonance is

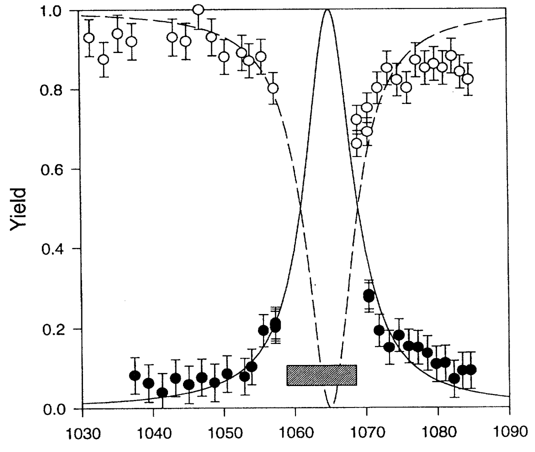

FIG. 1. IR spectrum of Ag_2NH_3 in the region of the NH_3 umbrella mode. The spectrum was obtained by monitoring the IRMPD depletion (4 J cm^{-1}) of Ag_2NH_3, (○) by monitoring the remaining Ag_2NH_3 through UV laser (308 nm) induced Ag_2 ($A\,^1\Sigma_u$) emission (see text), and (●) by monitoring the production of Ag_2 ($X\,^1\Sigma_g$) by LIF (431 nm). In both cases the photolysis and probe lasers counterpropagated coaxially with the probe beam diameter less than that of the photoanalysis beam and the probe laser following the photolysis laser by 60 μs. The IRMPD yield was obtained by normalization (○) to the emission signal obtained with only the UV laser operating and (●) to the LIF signal obtained in the absence of NH_3. The lines through the points are Lorentzian functions. The shaded bar marks a frequency gap in the line-tuned output of the $^{12}CO_2$ laser.

blueshifted in larger complexes (Ag_2NH_3, $n = 8, 9, 11, 14$, and 16), and there we were able to tune over complete Lorentzian bands [23].

DFT performs remarkably well in predicting the binding energy and IR properties we measure: calculated binding energy, 12.3 kcal mol^{-1}, cf. experimental value 14.7 ± 2 kcal mol^{-1}; calculated NH_3 umbrella mode frequency 1102 cm^{-1}, cf. our measurement of 1065 ± 5 cm^{-1}.

Comparison to extended metal surfaces.—Ammonia is known to chemisorb molecularly on Ag surfaces. It binds through the nitrogen lone pair with the symmetry axis perpendicular to the surface by electron donation to the surface [24,25]. Atop sites are favored. For Ag(110) the binding energy has been estimated as 11 kcal mol^{-1} [25]. The NH_3 umbrella frequency has been measured by electron energy loss spectroscopy to the 1050 cm^{-1} on Ag(110) [25]. The geometry, bond energy, and vibrational frequency we find for the complex are consistent with these surface values. End-on Ag_2NH_3 is a primitive model for atop binding to a silver surface. The second silver atom in the dimer affords the opportunity to compensate for repulsion in the entrance channel between the N lone pair and the Ag σ or surface s-band electrons by polarization of the electron density away from the binding site. This reduction in electron repulsion through polarization has been established as an important concept in metal atom reactions [26] and one that extends through metal dimers [12,14] to metal surfaces.

An aspect of the molecular view of photodissociation is that, in principle, one can account for *all* the electrons in the system and thereby the dynamics of particular adsorbate excitations can be isolated and explored. This is sometimes difficult to do for extended surfaces [27]. The electronic excitation of Ag_2NH_3 at 310 nm that we report here is interesting in that it is delocalized over the chemisorption bond *and* the metal dimer and is repulsive in the silver-ammonia coordinate. Photodesorption is the result of a prompt dissociation along a repulsive coordinate that provides the kinetic energy for desorption, excites internal modes of the metal and the desorbate (likely the ammonia umbrella motion due to the linear geometry), *and leaves electronic excitation in the metal.* Excitation of the umbrella motion in ammonia molecules photodesorbed from extended surfaces has been attributed to Rydberg-like excitation of the adsorbed molecule at around 5 eV [28]. Our work implies that a distinctly different excitation can have a similar dynamical consequence.

It is seen that, even at the dimer, many aspects of dynamics at surfaces are present in the photodissociation of metal cluster-ligand complexes. Of course, the dimer is not a surface, in particular, the rate of electronic quenching may be much slower. It will be fascinating to see how the electron-phonon coupling changes with cluster size. With this in mind we are extending these studies to larger silver clusters. Such studies are essential, as it has recently been pointed out, in that there are smaller and smaller differences in binding energy from site to site as the cluster size increases [28]. Only with larger clusters could we model realistically all aspects of bonding to extended surfaces.

The IRMPD of Ag_2NH_3 also has parallels in surface science literature. Laser induced thermal desorption is well studied [29] and resonant desorption has been the subject of active experimental and theoretical work. For both molecules and surfaces, the process is statistical; sequential absorption of IR photons is followed by rapid transfer of energy from the pumped mode [30]. Our experiments may be repeated with larger clusters at higher IR intensities and the question of the time scale of the transfer of vibrational energy from the "adsorbate" to the "bulk" may be directly measured.

In conclusion, experimental and theoretical studies on Ag_2NH_3 show that small metal cluster-ligand complexes share common features with the adsorbed state at metal surfaces, and have the advantage that particular adsorbate excitations can be isolated. The ensuing dynamics naturally proceed from a well-defined initial state. Such complexes are the natural fulfillment of the *cluster-surface analogy* introduced by Mutterties *et al.* [3]. We intend to extend these studies to larger clusters which may more closely mimic infinite surfaces. In this regard, this first study of thermal and photodissociation of a metal dimer-ligand complex is an important benchmark.

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