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Molecular beam studies of ammonia clustered with metals produced by pulsed laser reactive ablation

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Abstract

The results of spectroscopic studies of $\text{Me}(\text{NH}_3)_n$ clusters formed in the reaction of photoablated III group metal vapor with gaseous ammonia are reported here. The photoionization spectra of $\text{Me}(\text{NH}_3)$ clusters exhibit some features attributed to vibronic excitation of ionic clusters and transitions to autoionizing neutral Rydberg states. The first ionization potentials of these metals clustered with more than one ammonia molecule appear to decrease almost monotonically with increasing clusters size. The observed trend is consistent with a model in which the unpaired valence electron of the ground electronic state is delocalized in a well bound surface state. The data are confirmed by energetics and structure calculations performed by density functional method. (Int J Mass Spectrom 179/180 (1998) 319–326) © 1998 Elsevier Science B.V.

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1. Introduction

The study of neutral and ionized clusters has developed rapidly in recent years due to the unique capability of this state of matter to bridge the gap between isolated gas and condensed phase [1, 2]. The size dependent properties of these aggregates have been investigated by numerous spectroscopic methods [1–4]. Most studies were feasible because of cluster synthesis in molecular beam. Specific information on energetics, dynamic and structure of free clusters have been obtained from the supersonic expansion coupled

with laser techniques and time of flight mass spectrometry [1–6]. Recently a considerable interest has been developed in studies of metal atoms complexed with ammonia molecules. These systems are suitable models to investigate the interaction in metal-ligand bonding, metal-ion solvation and even in the absorption on metal surfaces and nitride deposition [7,8]. The existing studies of metal complexes with ammonia have been performed mainly on alkali, alkaline earth, and III group metal [6,9–11]. A limited number of other metal atoms have been studied as well [8]. Most investigations on alkali metal ammonia systems has been focused on the transition from metallic to non metallic properties, in which metal ammonia solutions undergo to low concentration of the alkali [12–18]. The metal in ammonia solution ionizes spontaneously, the Coulomb energy of the ionization

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

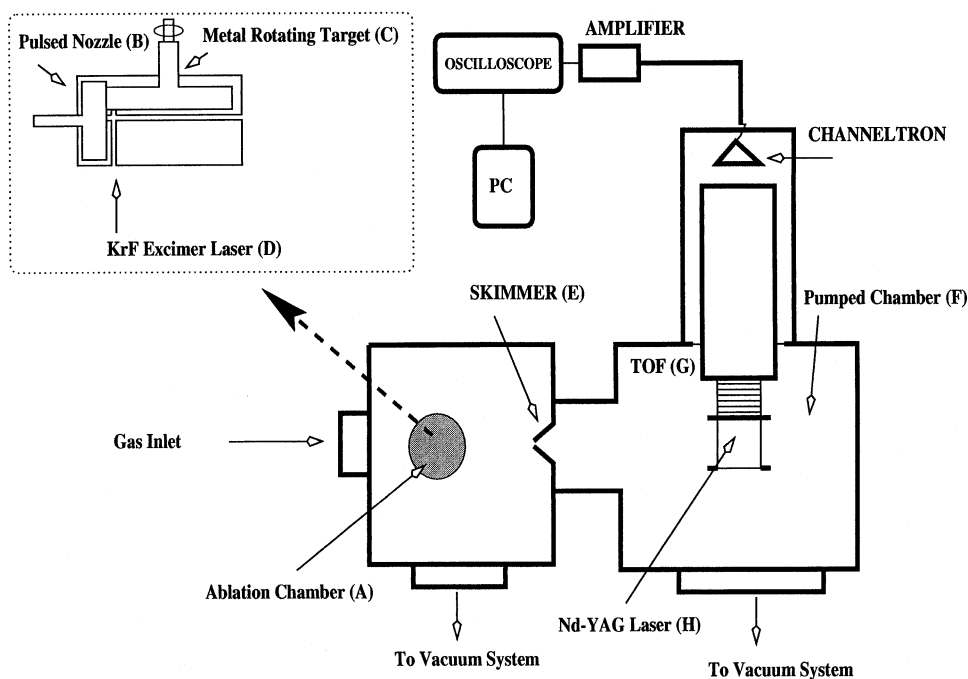


Fig. 1. Experimental apparatus.

process being compensated by the reorganization of polar solvent molecules around the dipolar charge distribution created by ionization [14]. It has been shown that as the number of ammonia molecules increases the unpaired valence electron of the metal is separated from the atom and trapped in a cavity surrounded by the polar solvent molecules so forming a solvated electron [13–18]. Studies of electron solvation in the bulk have a long history and in the past considerable progress has been made in treating the excess electron theoretically via the Feynman path integral and other computational techniques [15–19]. Experiments on the excess electron in polar solvent, such as ammonia and water, have been performed by photodissociation and photodetachment process in small gaseous clusters [6,9,10,20]. Photodissociations and photoionization spectra monitored as a function of cluster size have provided important information on the stabilization and charge distribution in a microcluster environment [5,6,9–11,20].

The present article starts with a short review of the work performed on III group atoms solvated by a small number of ammonia molecules. The details of

the photoionization spectra of the III group metal (Al, Ga, In) bonded to only one ammonia molecule in a wavenumber range of about 600 cm^{-1} above the threshold are reported subsequently. The spectra are interpreted on the basis that the excess energy, absorbed above threshold, can lead either to a specific ionic vibrationally excited state or to autoionizing states. The last part of the article is devoted to a discussion of the results of photoionization measurements of metals clustered with more than one ammonia molecule. The aim is to show that the NH_3 molecules have a characteristic behaviour in dissolving the bare atom and stabilizing the excess electron. Features observed are discussed in connection with DFT calculations of the structures and energetics of these clusters.

2. Methodology

2.1. Experimental

The experimental apparatus we have employed in this work is an instrument constructed in our labora-

tory and is shown in Fig. 1 [7]. It consists of two vacuum chambers separated by a 1 mm diameter 55° conical skimmer (Beam Dynamics). In a small ablation chamber (A) a mixture of ammonia ranging from 0.1% to 100% NH₃ in He at a stagnation pressure of $2 \div 4 \times 10^5$ Pa is introduced through a pulsed nozzle (200 μs time duration) of 1 mm diameter (B). A metal rotating target (C) is vaporized by 248 nm, 0.5 J/pulse KrF excimer laser (D). The formed plasma is entrained in the NH₃-He mixture and expanded into vacuum forming a supersonic jet. After being skimmed (E) the beam passes in a second differentially pumped chamber (F) and enters between the extraction plates of a time of flight mass spectrometer (G). The beam is there ionized by a Nd-YAG (Quantel) pumped dye laser (5 ns time duration) (H) whose fluence is kept low (few mJ) in order to avoid multiphoton ionization processes. The time of flight mass spectrometer resolution is $\Delta m/m \approx 200$. The ionization and excitation spectra of the clusters are measured by scanning the photon energy in the range 3 ÷ 5 eV using different dyes. The dye frequencies are doubled and when necessary also mixed with the residual 1064 nm radiation. Wavelengths calibration is performed with resonant transitions of atomic Al at 37700 cm⁻¹ of an atomic Fe at 34050 cm⁻¹. The data are corrected for the effect of the electric field of strength of 200 V/cm produced by the extraction plates of the TOF spectrometer. The apparent ionization potential of each ionized species is red shifted by $\Delta E = a\sqrt{F}$ where F stands for the applied field in V/cm and a is a fixed value. The a value depends on the nature of the starting state in the ionization transition, i.e. the ground state in the direct ionization, and Rydberg levels in the autoionizing processes [21–23]. Under our experimental conditions the ionization potential for the direct ionization is red shifted by 85 cm⁻¹ (0.01 eV) ($a = 6.1$) [23] while the a value for the autoionizing Rydberg levels is around 4 [23].

2.2. Computational

The ab initio density functional theory (DFT) method and pseudopotential approximation has been

used to determine the ground state energies, the geometries and the wave functions of neutral and ionic clusters. The standard B3LYP [24] functional was used to perform SCF calculations as implemented in the GAUSSIAN 94 program [25]. The cluster geometries are optimized using the 6-31g + (d) standard basis set on the Al atom and NH₃ molecules, and the 3-21g(d) on Ga and In atoms. The induction and dispersion energy components of the intermolecular interaction energy in Me(NH₃)_n are described with basis sets containing d and p gaussian functions on Al, N, Ga, and In atoms. For the last two atoms only the three valence electrons (ns²np¹) were considered during the calculation. The pseudopotential LANL2DZ function is used to take into account the core electrons shield effects [26]. In the geometrical optimization the equilibrium structures for both neutral and ionic clusters are obtained using the C_{3v} symmetry for Me(NH₃), C_{2v} for Me(NH₃)₂ and tetrahedral symmetry for Me(NH₃)₄. The vibrational frequencies are evaluated in the harmonic approximation by GF method [27].

3. Results and discussion

3.1. Near threshold photoionization spectra and structure calculations of Al, Ga, and In clustered with ammonia molecules

3.1.1. Me(NH₃)

The near threshold photoionization spectra of these group III metal clustered with one ammonia molecule show very similar behavior which can be interpreted with the help of structure calculations. In all three cases examined, the ionic yield increases as a function of the photon energy, and structures are observed in the spectra. It is known that in molecular photoionization the ionic yield may exhibit a rich structure near threshold and that in some cases its step function vibronic excitation behavior is obscured by a set of large bands [28]. Such bands reveal the occurrence of autoionizing phenomena from excited Rydberg states whose absorption cross section for excitation from the ground state are larger than those for direct excitation

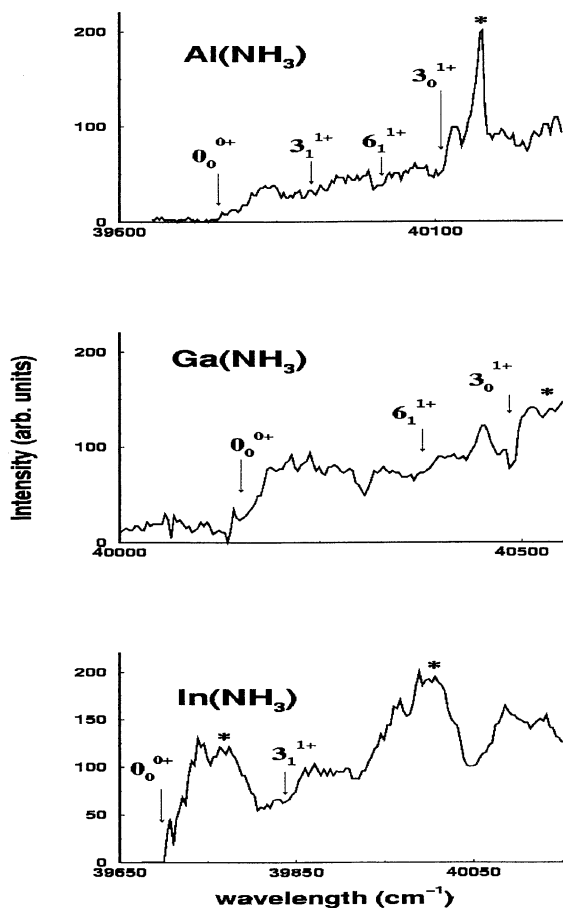


Fig. 2. Photoionization yield of Me(NH₃) near the ionization threshold.

[28,29]. We have interpreted the features in the spectra in terms of this picture.

The photoionization spectra of Me(NH₃) corrected for the direct ionization field effect are reported in Fig. 2 in a range of about 600 cm⁻¹ above the ionization threshold. The first step in each spectrum is associated with the $\Delta\nu = 0$ transition from the neutral complex to the vibronic ground state of the cation. It can be seen in Fig. 2 that the onset of one photon ionization process occurs at 39740 ± 20 cm⁻¹ for Al(NH₃), at 40170 ± 20 cm⁻¹ for Ga(NH₃) and 39700 ± 20 cm⁻¹ for In(NH₃). Other steps observed at higher energy are assigned to direct ionization leading to two excited vibrational levels of the ion, i.e. the ν_3 intermolecular ionic stretching vibration and

the ν_6 intermolecular ionic bending vibration. Other observed bands are attributed to highly excited Rydberg states, autoionizing to ionic vibrational levels with a propensity rule $\Delta\nu = -1$ [30]. It should be noted that the autoionizing band appears blue shifted with respect to the assigned ionic transitions because the field induced shift for the Rydberg levels is lower than for the direct ionization process [23].

In Al(NH₃) (Fig. 2) the onset of the 0₀⁰⁺ transition is red shifted by 8540 ± 20 cm⁻¹ with respect to the bare aluminum atom ($IP_{Al} = 48279$ cm⁻¹). The step observed at 39910 ± 20 cm⁻¹, blue shifted by about 170 cm⁻¹ with respect to the 0₀⁰⁺, can be identified with the transition involving the 3₁¹⁺ Al–N intermolecular stretching vibration, in agreement with calculations predicting the 3₁¹⁺ at about 145 cm⁻¹ [13]. The step at 40030 ± 20 cm⁻¹, shifted by about 290 cm⁻¹ with respect to 0₀⁰⁺ transition, can be attributed to the 6₁¹⁺ intermolecular degenerate bending transition estimated at around 300 cm⁻¹ [20]. The ionic yield rise at 40100 ± 20 cm⁻¹, shifted by about 360 cm⁻¹ with respect to the 0₀⁰⁺, may be attributed to the 3₀¹⁺ Al–N intermolecular stretching transition calculated around 330 cm⁻¹ [11]. The intense band very near the 3₀¹⁺ transition (marked with a star) may be assigned to high Rydberg autoionizing vibrational levels [21].

In Ga(NH₃) (Fig. 2) the 0₀⁰⁺ is red shifted by 8240 ± 20 cm⁻¹ with respect to Ga atom IP ($IP_{Ga} = 48380$ cm⁻¹) and few vibronic bands can be identified. A step at 40370 ± 20 cm⁻¹, shifted by about 230 cm⁻¹ with respect to the 0₀⁰⁺, may correspond to the 6₁¹⁺ intermolecular doubly degenerate bending transition estimated at around 258 cm⁻¹ [31]. The ionic yield increase at 40490 ± 20 cm⁻¹, shifted by about 350 cm⁻¹ with respect to the 0₀⁰⁺, can be attributed to the 3₀¹⁺ Ga–N stretching transition estimated around 320 cm⁻¹. Other observed bands (also star marked) can be assigned to autoionizing transitions.

In In(NH₃) (Fig. 2) the onset of the IP is observed at an energy 39700 ± 20 cm⁻¹, 6970 cm⁻¹ lower than In atoms IP ($IP_{In} = 46670$ cm⁻¹). In the spectrum a small rise, blue shifted by about 150 cm⁻¹ with respect to the 0₀⁰⁺ vibronic transition may be attributed to the 3₁¹⁺ stretching mode of In–N estimated at around 120 cm⁻¹ above the cluster IP. An

Table 1
Structures and energetics of neutral and ionized Me(NH₃) clusters

	Al(NH ₃)	Al(NH ₃) ⁺	Ga(NH ₃)	Ga(NH ₃) ⁺	In(NH ₃)	In(NH ₃) ⁺
$R_{\text{Me-N}}(\text{\AA})$	2.36	2.26	2.54	2.40	2.68	2.56
$R_{\text{N-H}}(\text{\AA})$	1.01	1.01	1.01	1.02	1.02	1.02
$\theta_{\text{Me-N-H}}$	110.9	112.6	108.1	110.6	107.9	110.4
D_e (eV)	0.45	1.38	0.32	1.27	0.36	1.15
IP (eV)						
calc.	4.92		4.84		4.65	
exp.	4.93		4.98		4.92	
$D'_e - D''_e$ (eV)						
calc.	0.92		0.95		0.79	
exp.	1.07		1.02		0.86	
3_1^{1+} (cm ⁻¹)						
calc.	165		124		120	
exp.	170		—		150	
6_1^{1+} (cm ⁻¹)						
calc.	225		258		250	
exp.	290		230		—	
3_0^{1+} (cm ⁻¹)						
calc.	330		320		310	
exp.	360		350		—	

intense band starting at 39930 cm⁻¹ covers a frequency region of about 100 cm⁻¹. This large band, probably superimposed to the 6₁¹⁺ and 3₀¹⁺ vibronic transitions estimated respectively at around 250 and 310 cm⁻¹ above the 0₀⁰⁺, can be attributed to auto-ionizing transitions [21]. Mass Analyzed Threshold Ionization (MATI) experiments, very recently performed, confirm this interpretation of the bands [31].

In Table 1 the calculated structures, the energetics and the equilibrium geometry of the neutral and ionized Al(NH₃), Ga(NH₃) and In(NH₃) clusters are reported together with the calculated and measured IP values and the difference between the binding energies of the ionic and neutral cluster determined from the relation

$$\text{IP}_{\text{Me}(\text{NH}_3)} - \text{IP}_{\text{Me}} = D_{0\text{Me}(\text{NH}_3)} - D_{0\text{Me}(\text{NH}_3)^+}$$

It can be seen from Table 1 that the IP thresholds for the Me(NH₃) cluster are significantly lower than the known ionization potential of the ground-state atoms [32]. The red shift of the IP threshold of Me(NH₃) in comparison to the Me atoms indicates that the binding energy of the ionized clusters,

Me(NH₃)⁺, is higher than that of the neutral. It can therefore be deduced that the Me–N bond is stronger in the ionized cluster. Moreover the binding energy values measured for neutral and ionic clusters are much larger than the typical values found for VdW complexes [1, 2].

3.1.2. Me(NH₃)_n

Nonresonant one photon ionization TOF mass spectra of Me(NH₃)_n clusters (Me = Al, Ga, In, Cu, Fe, Cr) have been already reported [8,11]. As an example in Fig. 3 the nonresonant one photon ionization mass spectra of Al(NH₃)_n, Ga(NH₃)_n, In(NH₃)_n and the transition metal clusters Me(NH₃)_n measured at a fixed ionizing laser energy are shown. It can be seen that many clusters Me(NH₃)_n⁺ with n ranging up to 9 are observed for the reported systems. From previous measurements at a different ionizing laser wavelength it was deduced that the cluster IP appears to decrease by increasing the number of ammonia molecules in the cluster. The IP threshold has been measured for Al(NH₃)_n with n up to 13, for Ga(NH₃)_n

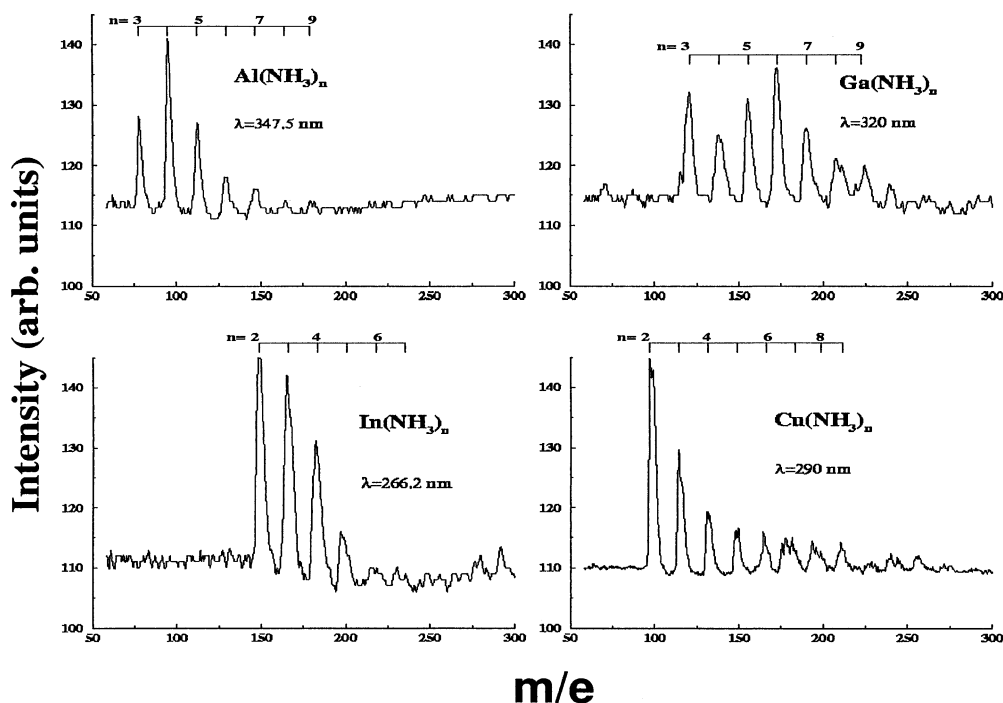


Fig. 3. $\text{Me}(\text{NH}_3)_n$ photoionization mass spectra (Me = Al, Ga, In, Cu).

and $\text{In}(\text{NH}_3)_n$ with n up to 3. The photoionization spectra are not structured and the rise of the signal intensity near the IP threshold is gradual over a wide range of wavelengths. This gradual IP onset can be due both to change in the cluster geometry upon ionization giving rise to poor Franck-Condon factors

and to the presence of various isomers with a slightly different IP. Calculated equilibrium geometrical parameters and experimental IP's for small neutral and ionic $\text{Me}(\text{NH}_3)_n$ are reported in Table 2. From the data a rapid IP cluster decrease up to $n = 3$ is observed in agreement with calculations. In Al for

Table 2

Structures and energetics of neutral and ionized $\text{Me}(\text{NH}_3)_n$ clusters ($2 \leq n \leq 4$)

n		$\text{Al}(\text{NH}_3)_n$	$\text{Al}(\text{NH}_3)_n^+$	$\text{Ga}(\text{NH}_3)_n$	$\text{Ga}(\text{NH}_3)_n^+$	$\text{In}(\text{NH}_3)_n$	$\text{In}(\text{NH}_3)_n^+$
	$R_{\text{Me-N}}(\text{\AA})$	2.39	2.28	2.45	2.37	2.60	2.53
2	$\theta_{\text{N-Me-N}}$	83.0	85.0	86.2	87.8	83.8	85.9
	IP (eV)						
	calc.	4.1		3.82		3.75	
	exp.	3.86		≤ 4.59		≤ 4.59	
3	IP (eV)						
	exp.	3.55		≤ 3.69		≤ 3.69	
4	$R_{\text{Me-N}}(\text{\AA})$	3.75	2.78	3.80	2.93	3.40	2.90
	IP (eV)						
	exp.	3.39		—		—	

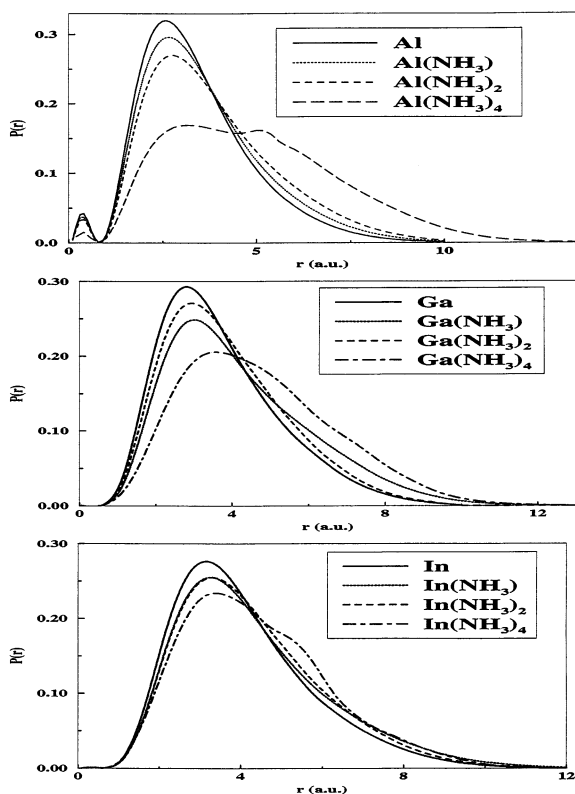


Fig. 4. Unpaired valence electron radial probability distribution functions versus distance from Me atom, for Al, Ga, In clustered with ammonia molecules.

$3 \leq n \leq 6$ the IP's decrease less rapidly and the decrease for $7 \leq n \leq 13$ is even slower [11].

The size dependent IP trend provides information on the Me and ammonia interaction which characterizes the structures of these aggregates. The different behavior identified in the IP decrease can be attributed to the different valence electron states according to previous solvation models [6,16,30]. In the first region a strong interaction between the metal and ammonia takes place. The system can be described by a one-center state having the electron very near the atom. The less rapid IP decrease for $n \geq 3$ suggests that the valence electron begins to be delocalized forming a surface Rydberg-like state. This hypothesis is confirmed by the calculated valence electron radial probability $P(r)$ of the $\text{Me}(\text{NH}_3)_n$ clusters (Fig. 4), which indicates that the valence electron density is

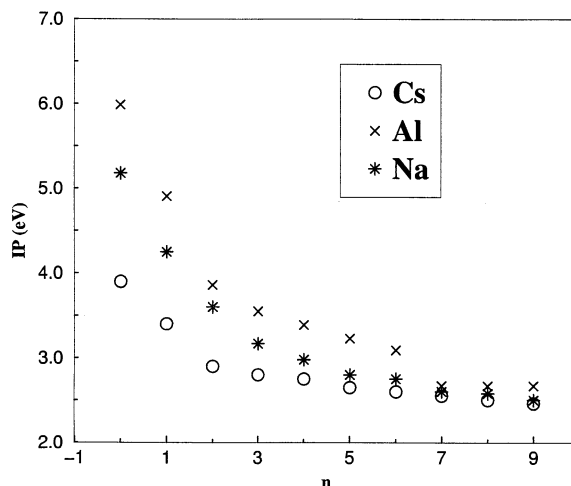


Fig. 5. Experimental ionization potential $\text{Me}(\text{NH}_3)_n$ (Me = Al [11], Na [34], Cs [5]) as a function of n .

concentrated very near the metal atom in the $\text{Me}(\text{NH}_3)$ and gradually becomes more diffuse for larger clusters. At large n an almost complete delocalization of the valence electron of the metal around NH_3 molecules should take place similarly for alkali ammonia clusters [30]. The IP of large clusters should go to the binding energies of an electron moving in a spherical potential originated by a Me^+ core screened by a dielectrical medium [6], and reach the bulk 1.45 eV value for the solvated electron [33]. A similar behavior was predicted for valence electron of alkali and alkaline earth metal ammonia clusters [30]. In Fig. 5 the measured IP's for Na, Cs, and Al clustered with ammonia molecules as a function of n are reported [5,11,34]. It can be seen that the IP of cluster with few ammonia molecules ($n \leq 4$) show a marked dependence on the type of metal, while at large n they tend to the same value. These results confirm that for $\text{Me}(\text{NH}_3)_n$ with very large n a complete solvation of valence electrons should take place not only for the alkali and alkaline earth metals as previously hypothesized, but also for the III group metals [11,16,17]. In $\text{Me}(\text{NH}_3)_n$ with $4 \leq n \leq 8$ the valence electron is predicted to be in a Rydberg-like state being squeezed out of an orbit close to the metal ion into an orbit where its density is predominantly associated with ammonia hydrogens. For larger $\text{Me}(\text{NH}_3)_n$ the elec-

tronic states are represented by the two center model [16] which describes the unpaired valence electron by an orbital localized far away from the cationic core.

In conclusion, we have shown that photon ablation of metals in presence of ammonia, under suitable conditions, gives rise to metal ammonia clusters. We have accurately measured the IPs of $\text{Me}(\text{NH}_3)$ clusters which are found to be lower by 1 eV with respect to that of the bare atoms. We have interpreted the photoionization spectra of third group $\text{Me}(\text{NH}_3)$ clusters through vibronic and autoionizing Rydberg transitions. We have obtained information on energetic and structure of these adducts. The experimental data are consistent with calculated values of binding energies of neutral and ionized $\text{Me}(\text{NH}_3)$ and $\text{Me}(\text{NH}_3)_2$. The measurement of the ionization potentials of $\text{Me}(\text{NH}_3)_n$ clusters shows that, when a third group metal is surrounded by a larger number of ammonia molecules, its valence electron tends to be separated from the atom and form a solvated electron, as already observed for alkali and alkaline earth metals.

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