Eur. Phys. J. D **4**, 225–229 (1998)

THE EUROPEAN
PHYSICAL JOURNAL D

Photoionization thresholds and structures of third group metals clustered with ammonia

T.M. Di Palma, A. Latini, M. Satta, and A. Giardini-Guidoni[a]

Dipartimento di Chimica, Università “La Sapienza”, P.le A. Moro, 5 00185 Roma, Italy
and
CNR, Istituto Materiali Speciali, via S. Loja, Tito Scalo (PZ), Italy

Received: 16 February 1998 / Revised and Accepted: 7 May 1998

Abstract. A photoionization study of the Me(NH_3) clusters formed in the reaction of photoablated third group metal vapor with gaseous ammonia is reported. The photoionization spectra exhibit some features due to vibrational excitation of ionic clusters and to transitions to neutral Rydberg states leading to autoionization. DFT quantum chemical calculations are performed on the Me(NH_3). The cluster geometries are fully optimized imposing the C_{3v} symmetry. The calculated values of the IPs are in agreement with those experimentally determined.

PACS. 33.80.Eh Autoionization, photoionization, and photodetachment – 42.62.Fi Laser spectroscopy – 36.40.-c Atomic and molecular clusters

1 Introduction

The study of metal atoms complexed with different solvating agents has received much attention in recent years. These systems provide, in fact, suitable models to understand metal ligand interaction and metal ion solvation [1–7]. The introduction of supersonic expansion techniques [8] coupled with laser spectroscopy allows to obtain detailed information on energetics and dynamics of these systems. Metal clusters composed of a third group element, such as Al, Ga or In atoms and solvent molecules like ammonia have been the subject of recent investigations because of their importance in the study of nitridation process and electron solvation [9–12]. Recently we have investigated the solvation phenomena in Al$(NH_3)_n$ gaseous clusters and shown that the ionization potentials (IPs) of clusters decrease with n [13]. This trend appears to be consistent with a model in which the metal valence electron, as n increases, is gradually transferred to a solvent cluster and an ion pair state in which both the Al^+ ion and the electron are surrounded by ammonia molecules is formed [12,13]. In case of small cluster ($n < 3$), calculations indicate that the valence electron is still localized near the metal ion, and that the one center model is valid in describing the structure of the complexes [6,7,14]. A strong red shift of the cluster IP with respect to the IP of the bare atom has been found [11,13]. This effect can be ascribed to the weaker interaction between the NH_3 lone pair and the valence electron of the metal for the neutral cluster with respect to the strong interaction between NH_3 and the ionized metal.

The present paper reports further experimental data on laser ionization spectroscopy of Al and other small clusters of the third group metals, in particular of Ga and In, solvated by one ammonia molecule. The photoionization spectra are measured in a wavenumber range of 900 cm^{-1} above the threshold. They are interpreted on the basis that one photon absorption can lead either to specific ionic vibrationally excited states or to neutral autoionizing states. DFT quantum chemical calculations, performed on these systems, are in agreement with the experimental results.

2 Experimental

The clusters apparatus used for these experiments is basically identical to that previously described [9,10,15]. A beam of ammonia seeded in Ar at a stagnation pressure of 4×10^5 Pa is introduced through a pulsed valve in a small chamber. In the same chamber an excimer laser vaporizes a rotating metal target. Vaporized atoms are mixed with the seeded beam and are expanded into vacuum through an exit channel forming a supersonic jet. The jet, after being skimmed, travels 30 cm and it is ionized by a Nd–YAG pumped dye laser operating in the photon energy range 28 700−41 000 cm^{-1}. Wavelength calibration is performed with resonant transition of atomic Al at 37 700 cm^{-1} and of atomic Fe at 34 050 cm^{-1}. The laser fluence is kept low to avoid multiphoton ionization so that only photoions formed by one photon process are selected by a time of flight mass spectrometer (TOF) and detected by a channeltron. The cluster ion yield is measured by scanning the photon energy. The data are corrected for the effect of the electric field, of strength $E_z = 200$ V/cm, produced by the extraction plates of the TOF mass spectrometer.

---

[a] e-mail: `giardini@axrma.uniroma1.it`

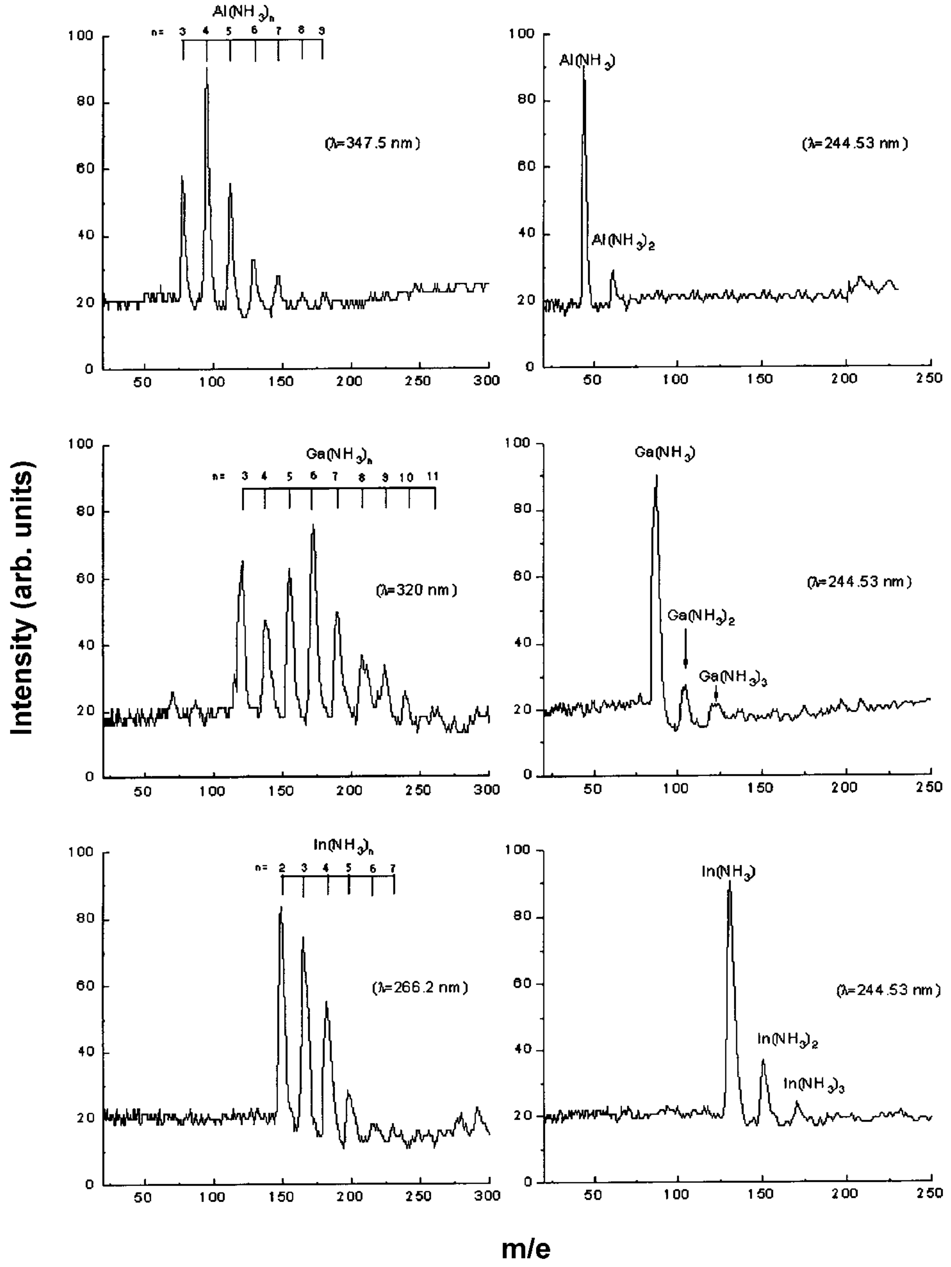

Fig. 1. Non resonant one photon ionization TOF mass spectra of Me(NH$_3$)$_3$ clusters taken at laser fluence of 0.2 mJ/cm^2. The wavelength used in the ionization process are reported at the top of each mass spectrum.

As a result the apparent ionization potential of the species is red shifted by $\Delta E = aF^{1/2}$, where F is the electric 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, Rydberg levels in the autoionization process [16–18]. Under our experimental conditions the ionization potential is red shifted by 85 cm^{-1} (0.01 eV), being $a = 6.1$. For the autoionizing Rydberg levels a falls between 2 and 4 [17].

3 Result and discussion

3.1 Mass spectra

Figure 1 displays typical non resonant one photon ionization TOF mass spectra of Me(NH$_3$)$_n$ clusters obtained at laser fluence of about 0.2 mJ/cm^2 and by setting different wavelengths. It can be seen that at high wavelengths (Fig. 1a) only clusters with $n \geq 2$ are ionized and detected since this photon energy is not high enough to ionize small clusters. By decreasing the laser wavelength (Fig. 1b) also the ionic signal due to Me(NH$_3$) clusters is observed in the mass spectrum. Furthermore the ionic yield of large clusters is very small. This can be due to the fact that when the photon energy absorbed by the cluster in the ionization process is in large excess with respect its IP, fragmentation can occur [12,15].

3.2 IP threshold spectroscopy

In Figure 2 the above threshold photoionization spectra of Al(NH$_3$), Ga(NH$_3$), In(NH$_3$), corrected for the field ionization effect, are reported. In all the three cases examined the ionic yield increases as a function of the photon energy, and the spectra exhibit some structures. It is well-known that in molecular photoionization the ionic yield may exhibit a rich structure near threshold an that in some cases its step function vibronic excitation behavior is obscured by a set of large bands [19]. Such bands reveal the presence of autoionizing phenomena from excited Rydberg states whose absorption cross-section for excitation from the ground state are larger than absorption cross-section for direct excitation [19,20]. We have interpreted the features in the spectra in terms of this picture. The first step in each spectrum is associated with the $\Delta v = 0$ transition from the neutral complex to the vibronic ground state of the cation *i.e.* according to the spectroscopic notation $\nu_{\nu''}^{\nu'}$. It can be seen from the Figure 2 that the onset of one photon ionization process occurs at $39\,740 \pm 20$ cm^{-1} for Al(NH$_3$), at $40\,170 \pm 20$ cm^{-1} for Ga(NH$_3$) and $39\,700 \pm 20$ cm^{-1} for In(NH$_3$). Other steps observed at higher energy are assigned to direct ionization leading to excited vibrational level of the ion; in particular the ν_3 intermolecular ionic stretching vibration and the ν_6 intermolecular ionic bending vibration. Other bands are attributed to high excited Rydberg states autoionizing to ionic vibrational levels with a propensity rule $\Delta v = -1$ [21].

In Al(NH$_3$) (Fig. 2a) the onset of the $0_0^{0^+}$ transition is red shifted by $8\,540 \pm 20$ cm^{-1} with respect to the bare aluminum atom ($IP_{\rm Al} = 48\,279$ cm^{-1}). A second step is observed at $39\,910 \pm 20$ cm^{-1} blue shifted by about 170 cm^{-1} with respect to the $0_0^{0^+}$. This step can be identified with the $3_1^{1^+}$ transition involving the Al–N intermolecular stretching vibration, in agreement with calculations that predict the $3_1^{1^+}$ at about 145 cm^{-1} [13]. The step at $40\,030 \pm 20$ cm^{-1}, shifted by about 290 cm^{-1} with respect to $0_0^{0^+}$ transition, can be attributed to the $6_1^{1^+}$ intermolecular degenerate bending transition estimated at around 300 cm^{-1} [16]. The rise at $40\,100 \pm 20$ cm^{-1}, shifted by about 360 cm^{-1} with respect to the $0_0^{0^+}$, may be attributed to the $3_0^{1^+}$ Al–N intermolecular stretching transition calculated around 330 cm^{-1} [13]. The intense band very near the $3_0^{1^+}$ transition may be assigned to high Rydberg autoionizing vibrational levels [22], converging to the $\nu_3^+ = 1$ intermolecular vibrational frequency. It should be noted that the autoionizing band appears blue shifted with respect to the $3_0^{1^+}$ transition, because the field induced shift for the Rydberg levels is lower than for the direct ionization process [18].

In Ga(NH$_3$) (Fig. 2b) the $0_0^{0^+}$ is red shifted by $8\,240 \pm 20$ cm^{-1} with respect to Ga atom IP ($IP_{\rm Ga} = 48\,380$ cm^{-1}) and few vibronic bands can be identified. A step at $40\,370 \pm 20$ cm^{-1}, shifted by about 230 cm^{-1} with respect to the $0_0^{0^+}$, may correspond to the $6_1^{1^+}$ intermolecular doubly degenerate bending transition estimated at around 258 cm^{-1} [22]. The rise at $40\,490 \pm 20$ cm^{-1}, shifted by about 350 cm^{-1} with respect to the $0_0^{0^+}$, can be attributed to the $3_0^{1^+}$ Ga–N stretching transition estimated around 320 cm^{-1}. A band near the $6_1^{1^+}$ is observed and, as for Al(NH$_3$), can be assigned to autoionizing transitions.

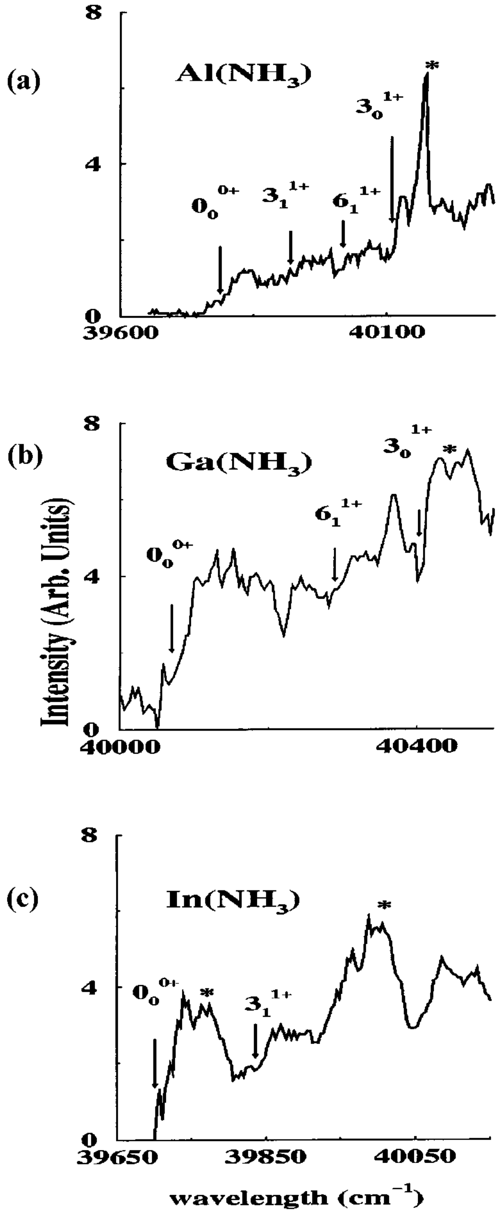

Fig. 2. Photoionization yield of Me(NH$_3$) near the ionization threshold recorded in an electrostatic field of 200 V/cm, using a frequency doubled laser dye. The wavenumbers are corrected by electrostatic field effect [22]. (a) Al(NH$_3$), (b) Ga(NH$_3$), (c) In(NH$_3$). Intermolecular vibronic transition are marked by arrows.

In In(NH$_3$) (Fig. 2c) the onset of the ion yield is observed at an energy $39\,700 \pm 20$ cm^{-1}, 6 970 eV lower than In atom IP ($IP_{\rm In} = 46\,670$ cm^{-1}). In the spectrum a small rise, blue shifted by about 150 cm^{-1} with respect to the $0_0^{0^+}$ vibronic transition may be attributed to the $3_1^{1^+}$ stretching mode of In–N estimated at around 120 cm^{-1} above the cluster IP. An intense band

Table 1. Calculated structures and energetics of neutral and ionized Me(NH_3) clusters.

		Al(NH_3)	Al(NH_3)$^+$	Ga(NH_3)	Ga(NH_3)$^+$	In(NH_3)	In(NH_3)$^+$
$R_{\mathrm{Me-N}}$ (Å)		2.36	2.26	2.40	2.30	2.60	2.50
$R_{\mathrm{N-H}}$ (Å)		1.01	1.01	1.01	1.02	1.02	1.02
$\theta_{\mathrm{Me-\widehat{N}-H}}$		110.9	112.6	108.1	110.6	107.9	110.4
D_e (eV)		0.45	1.38	0.63	1.84	0.61	1.64
IP (eV)	calc.	4.92		4.79		4.64	
	exp.	4.93		4.98		4.92	
$D_e^{'} - D_e^{''}$ (eV)	calc.	0.92		1.21		1.03	
	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		-	

starting at 39 930 cm^{-1} covers a frequency region of about 100 cm^{-1}; this band, probably overimposed to the $6_1^{1^+}$ and $3_0^{1^+}$ vibronic transitions estimated respectively at around 250 and 310 cm^{-1} above the $0_0^{0^+}$, can be attributed again to autoionizing transitions. Calculations and MATI experiments, very recently performed, confirm this interpretation of the bands [22].

3.3 Binding energies and structure calculations

Ab initio calculations of the structural parameters of the small neutral and ionic clusters Al$(NH_3)_n$ $n = 1, 2$ were previously performed and compared with measured values [13]. DFT method was used to determine the ground state energies, the geometries and the wave functions of both neutral and ionic clusters. Standard B3LYP functional was used to perform SCF calculations as implemented in the GAUSSIAN 94 program [23]. The aluminum cluster geometries were optimized using the 6-31g+(d) standard basis set. The vibrational frequencies were evaluated in the harmonic approximation by GF method [24]. For the first time the ground state energies and geometries of neutral and ionic Ga(NH_3) and In(NH_3) have been determined by using also B3LYP model [25]. To perform DFT calculations the standard 6-31g+(d) on the NH_3 atoms has been used together with the LAN2DZ basis set centered on Ga and In atoms. The Cartesian Gaussian wave functions for Ga and In have been determined by pseudopotentials [26].

In Table 1 the energetics and the equilibrium geometry of the neutral and ionized Al(NH_3), Ga(NH_3) and In(NH_3) clusters are reported. The measured IP values and the difference between the binding energies of the ionic and neutral cluster determined from the relation

$$IP_{\mathrm{Me(NH_3)}} - IP_{\mathrm{Me}} = D_{o\,\mathrm{Me(NH_3)}} - D_{o\,\mathrm{Me(NH_3)^+}}$$

are also shown. The agreement between the measured and calculated values is quite good for Al and reasonable for Ga and In. (The difference between the ground and ionized zero point energy has been neglected).

From the results reported in Table 1 it can be deduced that these third group metals can form quite stable compounds when bound to ammonia. In fact both the Me–N equilibrium distances and the binding energies indicate that the intermolecular forces between Me and NH_3 are stronger than the purely dispersive ones. A detailed analysis of the bonding mechanisms shows that molecular stability is due to polarization and charge transfer energies, dominating over higher order, charge redistribution effects [27]. It should be noted that these large binding energies support our previous hypotheses that these complexes can be gaseous precursors in the nitridation processes [9].

In summary in this paper new spectroscopic information on Al, Ga, In–ammonia clusters have been reported. We have measured for the first time the IP of Me(NH_3) cluster which is found to be around 1 eV lower than that for the metal atom. We have interpreted the photoionization spectrum of these systems through vibronic and Rydberg autoionizing transitions. The experimental data are consistent with calculated values of binding energies of neutral and ionized Me(NH_3) clusters.

This work has been supported by CNR Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II and Murst.

References

1. M. Trenary, H.F. Schraefer III, J. Chem. Phys. **68**, 4047 (1978).
2. M. Trenary, H.F. Schaefer III, P. Kollman, J. Am. Chem. Soc. **99**, 5833 (1990).

3. M. Marchi, M. Sprik, M.L. Klein, J. Phys. Cond. Matter **2**, 5833 (1990).
4. G. Lepoutre, J. Jortner, J. Phys. Chem. **76**, 683 (1972).
5. R.N. Barnett, U. Landman, C.L. Cleveland, N.R. Kestner, J. Jortner, Chem. Phys. Lett. **148**, 249 (1988).
6. R.N. Barnett, U. Landman, C.L. Cleveland, N.R. Kestner, J. Jortner, Chem. Phys. Lett. **145**, 382 (1988).
7. R.N. Barnett, U. Landman, Phys. Rev. Lett. **70**, 1775 (1993).
8. M.D. Morse, M.E. Gensac, J.R. Heath, R.E. Smalley, J. Chem. Phys. **83**, 2293 (1985).
9. T.M. Di Palma, A. Latini, A. Giardini Guidoni, A. Mele, S. Piccirillo, V. Marotta, A. Santagata, Nucl. Inst. Meth. Phys. Res. B **122**, 415 (1997).
10. A. Giardini Guidoni, A. Mele, T.M. Di Palma, M. Coreno, R. Teghil, A. Morone, Appl. Surf. Sci. **106**, 154 (1996).
11. I.V. Hertel, C. Hüglin, C. Nitsch, C.P. Schultz, Phys. Rev Lett. **67**, 1767 (1991).
12. C.P. Shulz, R. Hangstätter, H.U. Tihes, I.V. Hertel, Phys. D Atoms **10**, 279 (1988).
13. T.M. Di Palma, A. Latini, M. Satta, M. Varvesi, A. Giardini-Guidoni, Chem. Phys. Lett. **284**, 184 (1998).
14. G.J. Martina, L.M. Klein, J. Phys. Chem. **95**, 515 (1991).
15. S. Piccirillo, M. Coreno, C. Bosman, A. Giardini Guidoni, A. Mele, A. Palleschi, Chem. Phys Lett. **247**, 577 (1995).
16. D.R. Rodham, G.A. Blake, Chem. Phys. Lett. **264**, 522 (1997).
17. R. Linder, H.J. Dietrich, K. Muller-Dethlefs, Chem. Phys. Lett. **228**, 417 (1994).
18. F. Remacle, R.D. Levine, J. Chem. Phys. **107**, 3382 (1997).
19. A.L. Sobolewski, W. Domcke, J. Chem. Phys. **86**, 176 (1987).
20. Y. Ono, S.H. Lin, H.F. Prest, C.Y. Ng, E. Miescher, J. Chem. Phys. **73**, 4855 (1980).
21. S. Berry, J. Chem. Phys. **45**, 1228 (1966).
22. M. Satta, Ph.D. thesis, Università degli studi di Roma La Sapienza A.A. 1996/97 .
23. Gaussian 94, Revision D.2, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
24. E.B. Wilson, J.C. Decius, P.C. Cross, *Molecular Vibrations* (Mc. Graw-Hill, 1990).
25. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
26. P.J. Hay, W.R. Wadt, J. Chem. Phys. **82**, 270 (1985).
27. S. Kolman, J. Compt. Chem. **65**, (1985).