Chemical Physics Letters 706 (2018) 736–740

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Editor's choice

Infrared spectroscopy of $Ca(NH_3)_n$ complexes

Munirah D. Albaqami, Andrew M. Ellis [*]

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

ARTICLE INFO

Article history:
Received 30 April 2018
In final form 22 June 2018
Available online 26 June 2018

ABSTRACT

Infrared spectra of $Ca(NH_3)_n$ complexes in the gas phase have been recorded for the first time. The spectra are consistent with structures where the Ca atom resides inside one or more solvation shells of NH_3 molecules. IR spectra were recorded using a photodissociation technique. A comparison of the spectra with those predicted from *ab initio* calculations suggests that $Ca(NH_3)_8$ has all NH_3 molecules in a single solvent shell around the Ca atom, whereas the spectra of $Ca(NH_3)_9$ and $Ca(NH_3)_{10}$ are consistent with two-shell structures.

1. Introduction

The study of metals dissolved in liquid ammonia has a history stretching back to original work by Humphry Davy in the early 19th century [1]. Davy was the first to see the remarkable colours of alkali/ammonia solutions, which range from metallic bronze at high metal concentrations to deep blue at low concentrations. It is now known that the blue colour results from the formation of solvated electrons, whereas the highly reflective bronze sheen derives from metallic-like solutions with large electrical conductivities. There have been various attempts over many decades to learn more about these solutions. However, as described in a relatively recent review article [2], these are complex solute/solvent systems and the full range of species active in these solutions is poorly understood.

Detailed information about solute-solvent interactions is difficult to extract from a multi-component bulk solution. An alternative way of learning something about the underlying interactions between metal atoms and ammonia molecules is through the study of small metal-ammonia complexes in the gas phase. Spectroscopic techniques, such as mass-selective laser spectroscopy, can be used to determine the structures adopted by such complexes. Furthermore, quantum chemical calculations on relatively small complexes are viable and their combination with spectroscopic measurements is a particularly powerful way of exploring solute-solvent interactions.

In the case of alkali metals, the earliest experimental studies of $M(NH)_n$ complexes employed photoionization mass spectrometry, and in particular the measurement of ionization energies as a function of n [3–7]. Unfortunately mass spectrometry provides limited structural information and so more recent work has exploited optical spectroscopy, including resonance-enhanced multiphoton ionization spectroscopy and photodepletion spectroscopy [8–14]. Other experimental techniques, such as photoelectron spectroscopy [15] and electric deflection measurements [16], alongside various theoretical studies [17–21], have provided a considerably detailed picture of the solvation of alkali atoms by ammonia molecules.

By comparison with the alkali metals, complexes between alkaline earth metals and ammonia have received scant attention. In fact until very recently the only study was restricted to $Mg(NH_3)_n$, and in particular photoionization measurements and associated *ab initio* calculations [22]. In marked contrast to alkali-ammonia complexes, where the alkali metal is surrounded by ammonia molecules (which we will call an interior complex) in the lowest energy structure, $Mg(NH_3)_n$ complexes adopt a surface structure in which the Mg atom sits on the surface of an $(NH_3)_n$ cluster. A surface location is favoured energetically because the closed shell ground state of the Mg atom interacts rather weakly with individual NH_3 molecules, and so there is no energetic gain in disrupting the hydrogen bonding in the ammonia network. This observation most probably explains the very low solubility of magnesium in liquid ammonia [23].

By way of contrast Ca, Sr and Ba all readily dissolve in liquid ammonia and generate solvated electrons in sufficiently dilute solutions [24]. This suggests that these heavier alkaline earth metals have a stronger interaction with ammonia molecules. To probe this interaction, we report here the first infrared (IR) spectra of alkaline earth-ammonia complexes, focusing on $Ca(NH_3)_n$. The IR spectra were recorded in the NH stretching region using a photodepletion technique. As will be described, only complexes with sufficiently low ammonia binding energies, which correspond to relatively large complexes, yield IR depletion spectra. We are able

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[*] Corresponding author.
E-mail address: andrew.ellis@le.ac.uk (A.M. Ellis).

https://doi.org/10.1016/j.cplett.2018.06.048
0009-2614/

to show that these spectra are consistent with interior structures where the Ca atom is surrounded by ammonia molecules.

2. Experimental

The apparatus employed has been described in detail previously [11]. Briefly, $\text{Ca(NH}_3)_n$ complexes were made by laser ablation of the solid alkaline earth metal in an atmosphere of pure ammonia. The ammonia was delivered by a pulsed valve and flowed over the surface of the metal target at a typical pressure of 2 bars before expanding into vacuum to generate a supersonic jet. The laser pulse was provided by a Nd:YAG laser operating at 532 nm and was synchronized to arrive at the metal target at the same time as the pulse of ammonia gas. We used pure ammonia, rather than ammonia seeded into an inert carrier gas, as the former gives much stronger spectroscopic signals. However, this improved signal comes at the expense of poorer cooling in the supersonic expansion, although we have no means of directly measuring the temperature of the gas.

The jet was then skimmed to form a molecular beam and entered the source region of a Wiley-McLaren time-of-flight mass spectrometer, where it was crossed by two pulsed laser beams. One laser, operating in the ultraviolet, was used for photoionization of the complexes. The other laser pulse, timed to arrive just before the ultraviolet pulse, was used to excite spectroscopic transitions in the infrared (from a LaserVision optical parametric oscillator/amplifier). IR absorption was achieved by a form of action spectroscopy involving the dissociation of $\text{Ca(NH}_3)_n$ following photon absorption, usually by loss of a single NH_3 molecule. The dissociation event can be registered through a fall in the $\text{Ca(NH}_3)_n^+$ signal measured via the mass spectrometer. In this sense the spectroscopy is mass selective.

However, there are two potential complications to note. First, if the IR photon energy is below the dissociation energy of the complex, and/or the dissociation process is very slow, then photodepletion spectroscopy is not viable. Second, any loss in $\text{Ca(NH}_3)_n^+$ signal casued by photodissociation of $\text{Ca(NH}_3)_n$ can be countered by new signal for $\text{Ca(NH}_3)_n^+$ created from photodissociation of $\text{Ca(NH}_3)_{n+1}$, assuming both neutral complexes absorb at the same IR wavelength. To try and minimise the effects of this potential clash of opposing signals, we have deliberately adjusted the expansion conditions in the current series of experiments such that the $\text{Ca(NH}_3)_n^+$ ion signal is significantly larger than the $\text{Ca(NH}_3)_{n+1}^+$ signal prior to any addition of IR radiation. Under these conditions any signal enhancement from dissociation of $\text{Ca(NH}_3)_{n+1}$ registered in the $\text{Ca(NH}_3)_n^+$ mass channel should be smaller than the depletion in the same mass channel derived from absorption by $\text{Ca(NH}_3)_n$.

3. Computational details

To support the experimental work, *ab initio* calculations were performed on a series of $\text{Ca(NH}_3)_n$ complexes. These calculations employed second-order Møller-Plesset perturbation theory (MP2) in conjunction with 6-311++G(d,p) basis sets on the atoms. This basis set was selected because it is reasonably large and flexible without being too computationally demanding for the relatively large complexes considered in this work. The calculations used GAUSSIAN 03 software [25].

In addition to predicting equilibrium geometries, IR spectra were also calculated for each complex considered. The theoretical spectra were based on the harmonic approximation but employed a scaling factor to partly account for anharmonic effects on the band positions. This was obtained from a comparable calculation on a single NH_3 molecule and choosing a scaling factor (0.936) which brought theory and experiment into best agreement. This scaling factor was then applied to $\text{Ca(NH}_3)_n$ vibrational predictions.

4. Results and discussion

Fig. 1(a) shows a photoionization mass spectrum recorded for $\text{Ca(NH}_3)_n$ in the absence of the IR laser beam. Under the conditions used the highest intensity occurs for $\text{Ca(NH}_3)_8^+$ and then declines for higher mass species. In fact the $\text{Ca(NH}_3)_8^+$ ion shows a relatively high abundance under a wide variety of experimental conditions (different NH_3 stagnation pressures, valve opening-ablation laser delays, and UV wavelengths), suggesting that this ion is particularly stable (a magic number ion).

Fig. 1(b) shows a mass spectrum recorded under the same conditions but now with the IR radiation added. The IR output was fixed at 3153 cm^{-1} for this measurement, a position which overlaps with one of the broad absorption bands seen for several complexes (see later). A pronounced change in the mass spectrum occurs, with clear evidence of neutral $\text{Ca(NH}_3)_n$ photodissociation leading to signal enhancement in lower mass channels at the expense of signal in higher mass channels. We can therefore use this signal depletion to record IR spectra of neutral clusters and Fig. 2 shows some examples. For simplicity we will refer to the spectrum collected by detecting $\text{Ca(NH}_3)_n^+$ as being from the neutral $\text{Ca(NH}_3)_n$ species. In fact we expect this neutral complex to be the dominant contributor but we cannot rule out some contribution from larger species, not least because photoionization may lead to the loss of one or more NH_3 molecules.

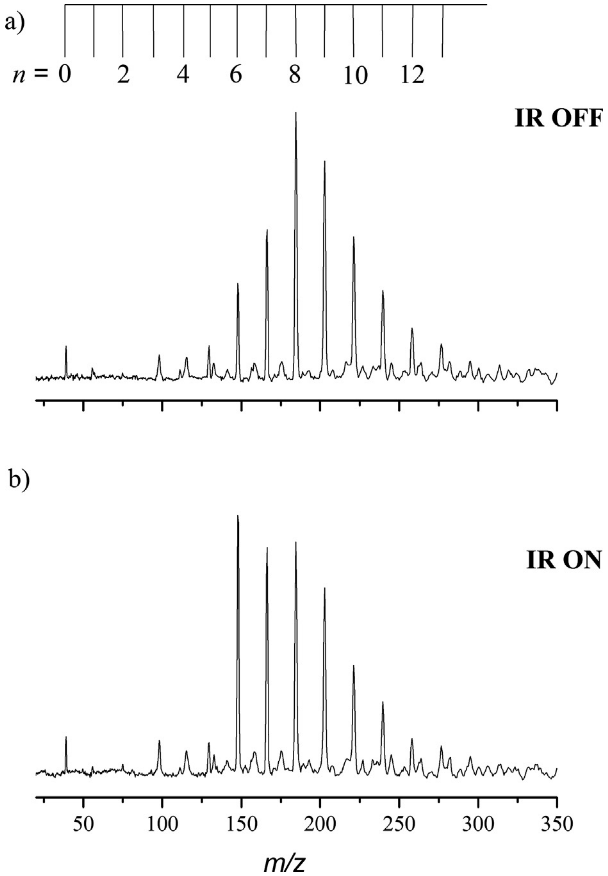

Fig. 1. Photoionization mass spectra obtained for $\text{Ca(NH}_3)_n$ at a laser wavelength of 346 nm. Spectrum (a) was obtained in the absence of the IR laser whereas spectrum (b) was recorded in the presence of the IR laser operating at 3153 cm^{-1}.