Infrared spectroscopy of closed *s*-shell gas-phase $M^+(N_2O)_n$ ($M = Li, Al$) ion–molecule complexes

*Ethan M. Cunningham, Alexander S. Gentleman, Peter W. Beardsmore & Stuart R. Mackenzie**

Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory,
South Parks Road, Oxford OX1 3QZ, United Kingdom

ORCID:

Ethan M. Cunningham: 0000-0001-5954-3083

Alexander S. Gentleman: 0000-0003-3830-2488

Stuart R. Mackenzie: 0000-0002-3166-8631

Dedication

This article is dedicated to Professor Tim Softley, FRS on the occasion of his 60th birthday. SRM will forever be grateful to Tim for his inspirational supervision and continued support over the years.

*corresponding author stuart.mackenzie@chem.ox.ac.uk

Abstract

We present the results of a combined experimental and computational study of the structures of gas-phase $M^+(N_2O)_n$ ($M = \text{Li, Al}$) complexes. Infrared spectra were recorded in the region of the N_2O asymmetric ($N=N$) stretch using photodissociation spectroscopy employing the inert messenger technique. Unlike in our previous studies on $M^+(N_2O)_n$ ($M = \text{Cu, Ag, Au}$ and $M = \text{Co, Rh, Ir}$) complexes, N- and O-bound isomers in this case are near isoenergetic and are not distinguished spectroscopically at this resolution. In the case of Li^+ complexes, there is, however, evidence for the presence of bound N_2 moieties, indicating the presence of inserted, $\text{OLi}^+\text{N}_2(\text{N}_2\text{O})_n$ -type structures. The weak N_2 band lies to the blue of the signature of molecularly N- and O-bound ligands and is well-reproduced in the simulated spectra of energetically low-lying structures computed from density functional theory. No such inserted isomers are observed in the case of $\text{Al}^+(\text{N}_2\text{O})_n$ complexes whose infrared spectra can be understood on the basis of molecularly-bound N_2O ligands. The differences in $M^+(\text{N}_2\text{O})_n$ structures observed for these closed-shell, ns^2 , metal centres relative to other metal cations are discussed in terms of the likely bonding motifs.

1. Introduction

Nitrous oxide (N_2O) is a known greenhouse gas[1,2] with a warming potential 300 times greater than carbon dioxide and accounts for 5% of the total anthropogenic greenhouse emissions. Furthermore, tropospheric N_2O emissions are the major source of stratospheric NO_x and dominate ozone depletion in the 21st century.[1,2] A wide range of human activities from manufacturing, fossil fuel use and agriculture, is driving annual N_2O level rises of 0.5-0.9 ppb per volume.[3]

Metal cations, in particular alkali metals Na and K, are also atmospherically significant. Hundreds of tons of meteoritic material, rich in light metals enter the upper atmosphere every day. The metals become a sink for positive charge and can be used as a tracer for the study of dynamics and the neutral/ion chemistry of the mesosphere and lower thermosphere (MLT).[4-10]

Metal-catalysed N_2O chemical reduction[11,12] is an effective route to reduce N_2O emissions and has been an active area of research in heterogeneous catalysis and cluster science.[13] $\text{M}^{+/0/-}(\text{N}_2\text{O})_n$ complexes in general represent model entrance-channel species for such reactions, in which the fundamental interactions involved can be studied in isolation.[14] Böhme and coworkers performed a detailed study of N_2O reactions with atomic transition metal cations,[15] while the role of atomic and cluster ions as single-site catalysts has been reviewed by Böhme and Schwarz.[3] Relevant binding interactions of metal atoms with N_2O have been studied both theoretically[16-18] and experimentally,[19,20] and reactivity studies of charged metal clusters with N_2O have been carried out under thermal and single-collision conditions[21-30] and spectroscopically.[31-33] Photoelectron spectroscopy measurements of metal monoxides, MO ($\text{M} = \text{Li}, \text{Na}, \text{K}$) utilised N_2O reactions with metal atoms as sources of metal monoxides.[34]

This group has recently reported spectroscopic studies of coinage metal and group 9 cation $\text{M}^+(\text{N}_2\text{O})_n$ complexes, combining infrared photodissociation (IRPD) spectroscopy with quantum chemical calculations to identify structural binding motifs.[35,36] In both cases spectroscopically–distinct N– and O–bound ligands were identified, giving rise to a diverse range of structural isomers. In the case of the coinage metals, the spectra were dominated by ground, singlet–state isomers.

However, for the group 9 metal complexes, particularly for Rh^+ , the range of isomers identified included low-lying excited electronic states. This find was not unsurprising given the abundance of low-lying electronic states in the platinum group metals which makes them so useful in catalysis.

Beyond electrostatic interactions, the bonding within metal-nitrous oxide complexes has been well established[19] and is dominated by electron donation from the N_2O HOMO-1, 7σ orbital to the metal ion (especially partially-filled M^+ -centred $s\text{-}d_z^2$ hybrid orbitals). By way of testing this mechanism further, we report here a combined experimental and quantum chemical study of $\text{Li}^+(\text{N}_2\text{O})_n$ and $\text{Al}^+(\text{N}_2\text{O})_n$ complexes, aiming to investigate the fundamental binding mechanisms associated with metals without any occupied d orbitals. IRPD spectroscopy, employing the inert-messenger technique, has been applied to determine the structures of the title complexes. In a well-established method, to aid with the interpretation, the recorded spectra are compared with those simulated for energetically low-lying structures determined from density functional theory (DFT).[37-39]

2. Experimental and Computational Methodology

The instrument and technique employed in these studies have been described in detail in previous publications, so only brief details are given here here.[35,36,40] Gas-phase $\text{M}^+(\text{N}_2\text{O})_n$ ($\text{M} = \text{Li}, \text{Al}$) complexes along with their argon-tagged (or N_2 -tagged) counterparts are formed by 532 nm pulsed ablation of a rotating metal Li/Al alloy disc (1:9) in the presence of Argon or Nitrogen carrier gas seeded with 0.6% (1.46%) N_2O . The resulting molecular beam is skimmed and the positively-charged species are detected by reflectron time-of-flight mass spectrometry.[41] The cluster source and detection operates at 10 Hz. Pulsed infrared radiation tuneable in the $2150\text{-}2350\text{ cm}^{-1}$ region covering the asymmetric ($\text{N}=\text{N}$) stretch in nitrous oxide, is provided by an optical parametric oscillator/amplifier system (LaserVision). The infrared beam counter propagates with the molecular beam and spectra are collected using the “inert messenger” technique.[42-47] **Absorption of an**

infrared photon results in the loss of a weakly-bound Ar fragment from a photoexcited $M^+(N_2O)_n$ -Ar complex thus providing a mass spectrometric signature. Monitoring the fractional depletion of a $M^+(N_2O)_n$ -Ar complex as a function of infrared photon energy yields the infrared spectrum of the $M^+(N_2O)_n$ complex of interest.

To aid in assigning and interpreting the experimental data, the structures and simulated infrared spectra of energetically low-lying isomers were calculated using density functional theory (DFT). Calculations performed on the $M^+(N_2O)_n$ structures employed the B3PW91-D3 hybrid density functional[48,49] coupled with the aug-cc-pVDZ basis set.[50,51] All calculations were carried out using the Gaussian09 suite of programs.[52]

3. Results and Discussion

Figure 1 shows the time-of-flight mass spectrum illustrating the production of $Li^+(N_2O)_n$ and $Al^+(N_2O)_n$ complexes following the ablation of a Li/Al alloy disc (composition 1:9) in the presence of a pulse of argon carrier gas (backing pressure 6 bar) seeded with 0.6% N_2O . A range of $Li^+(N_2O)_n$ and $Al^+(N_2O)_n$ complexes along with their argon-tagged counterparts can be identified. Under the same conditions, Li^+ apparently clusters more effectively than Al^+ . This is reflected in the comparable signal intensities for $Li^+(N_2O)_n$ and $Al^+(N_2O)_n$ complexes despite the 9:1 Al:Li alloy ratio. Similarly, the $Li^+(N_2O)_n$ complex distribution peaks around $n = 4$ under these conditions whilst the $Al^+(N_2O)_n$ distribution peaks at $n = 1$ and falls monotonically with n thereafter. Crude control over the size distribution of complexes generated can be exerted using a combination of the total backing pressure and the partial pressure of N_2O .

3.1 $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ IRPD Spectra

Figure 2 shows the IRPD spectra for the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2\text{--}9$) complexes. The spectrum for the $n = 2$ complex is dominated by a strong feature at 2267 cm^{-1} and weaker features around 2245 cm^{-1} and 2294 cm^{-1} . All three bands are blue-shifted from the N=N stretching frequency of free N_2O at 2223.5 cm^{-1} .^[53] The spectra for the $n = 3, 4$ complexes are qualitatively similar to that for $n = 2$ but red-shifted by 8 cm^{-1} and 14 cm^{-1} , respectively. The $n = 5, 6$ spectra each exhibit one strong band centred at 2245 cm^{-1} and 2242 cm^{-1} , respectively. In addition to this main band, a new spectral feature appears in the spectra of the $n = 7\text{--}9$ complexes very close to the free N_2O band at 2223.5 cm^{-1} . The strongest band observed in all these spectra undergoes a smooth redshift from 2267 cm^{-1} ($n = 2$) to 2242 cm^{-1} ($n = 6$) before blue-shifting very slightly to 2245 cm^{-1} by $n = 9$.

The evolution of the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ spectra with n exhibits marked similarity with that for the $\text{Co}^+(\text{N}_2\text{O})_n\text{-Ar}$ and coinage metal $\text{M}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) complexes and a similar rationale can be applied to their understanding.^{[36][35]} First, it is informative to understand the binding of the $\text{Li}^+\text{N}_2\text{O}$ complex. Figure 3a presents the calculated potential energy surface (PES), $V(R, \theta)$ of the $\text{Li}^+\text{N}_2\text{O}$ complex. The putative global minimum structure is a linear Li^+NNO complex (*i.e.*, binding *via* the terminal N atom). However, a deep secondary minimum, only *ca.* 0.1 eV above the global minimum is also observed which corresponds to a near-linear Li^+ONN configuration, *i.e.*, bound *via* the O atom. These features are shown in Figure 3b, a plot of energy vs. Li-N-N bond angle where the N_2O geometry was allowed to relax. **As befits the dominant electrostatic interactions, two equivalent low energy minima are observed as the metal cation approaches the lone pairs on the N_2O O-atom. The barrier between the two minima is extremely small and we expect a quasi-linear structure experiencing wide-amplitude motion (up to $\pm 50^\circ$) in this coordinate.**

The O-bound and N-bound minima are separated by a large barrier to internal rotation of $> 0.8\text{ eV}$ with the zero-point energy of the T-shaped (90°) structure very close to the dissociation energy (*i.e.*, barely bound). As observed in our previous studies of $\text{M}^+(\text{N}_2\text{O})_n$ complexes,^[35,36] the rapid cooling which occurs within our free-jet expansion facilitates the trapping of excited isomeric

forms behind such barriers, leading to the possibility of a range of isomers with mixed N– and O–bound ligands. In most of our previous studies, however, (for Cu⁺, Ag⁺, Au⁺ and Co⁺, Rh⁺ and Ir⁺) the N–bound potential minimum is significantly deeper than the O–bound giving rise to a clearly resolved spectral signature of each.

In what follows, we adopt a notation $^{2S+1}M^+N^xO^y$ for a particular structure in which x and y represent integer values indicating the number of N– and O–bound N₂O ligands, respectively. Thus, $x + y = n$, and $^1M^+N^1O^1$ represents a singlet state isomer of $M^+(N_2O)_2$ with one N-bound ligand and one O-bound ligand.

Figure 4 shows the experimental IRPD spectrum of $[LiN_4O_2Ar]^+$ together with the simulated spectra of calculated energetically low-lying structures. We adopt the $[LiN_4O_2Ar]^+$ nomenclature with simple molecular formula to indicate that it is unclear whether the N₂O ligands bind molecularly and/or form inserted structures. The only energetically low-lying isomers of molecularly-bound isomers are singlet states. Other multiplicities were calculated but lie much higher in energy and are unlikely to be formed in our expansion. The $^1Li^+N^2$ isomer represents the global minimum structure, however $^1Li^+N^1O^1$ and $^1Li^+O^2$ lie very close in energy at 0.05 and 0.10 eV, respectively reflecting the near isoenergetic nature of the N– and O–binding. The $^1Li^+N^2$ structure cannot account for the three bands observed and we infer the presence of O–bound ligands (in the form of $^1Li^+N^1O^1$ and $^1Li^+O^2$ isomers) to account for the lower wavenumber band at 2245 cm⁻¹.

Unlike the group nine[36] and coinage metal complexes,[35] in which the spectral signatures of N– and O–bound ligands were well-resolved (separated by 118 cm⁻¹ in the case of Au⁺(N₂O)₂–Ar) in the case of Li⁺(N₂O)_{*n*}–Ar complexes the two lie very close in wavenumber. This reflects the almost isoenergetic nature of the $^1Li^+N^2$, $^1Li^+N^1O^1$ and $^1Li^+O^2$ structures. The binding mechanism for N–bound N₂O ligands has been well established[19,35,36] and is dominated by electron donation from the N₂O HOMO-1, 7σ orbital to the metal centre. The 7σ orbital is antibonding with respect to the N=N bond, which is thus strengthened slightly by this donation resulting in a spectral blue-shift of the corresponding fundamental band. Unlike for the group 9 and 11 cations Li⁺ does not possess any

occupied d orbitals, and the donation from the 7σ orbital is less efficient leading to a smaller blue-shift and reduced distinction between N– and O–bound ligands.

It is clear, however, that molecularly–bound isomers cannot fully account for the spectrum observed. Figure 4 also shows the lowest triplet state isomers, ${}^3\text{Li}^+\text{N}^1(\text{ins.})$ and ${}^3\text{Li}^+\text{O}^1(\text{ins.})$, in which the metal ion is inserted into the N_2O forming a $\text{OLi}^+\text{N}_2(\text{N}_2\text{O})$ structure. The triplet represents the lowest-energy multiplicity for all inserted isomers of all complex size, consistent with *ab initio* studies concluding the triplet, $\text{X}^3\Sigma^-$, state is the lowest energy term of LiO^+ .^[54] The 2294 cm^{-1} band agrees well with the simulated stretch from the N_2 moiety which becomes infrared allowed when the N_2 binds to a metal ion.^[55-57] The three bands in the observed spectrum are therefore assigned as a mixture of molecularly adsorbed N– and O–bound N_2O ligands, together with inserted isomers.

A similar rationale can be applied to assigning the bands in the observed spectrum for $[\text{LiN}_6\text{O}_3\text{Ar}]^+$ (Figure 5). The main band at 2259 cm^{-1} is almost certainly the signature of molecularly N–bound N_2O with the weak shoulder to the red edge O–bound N_2O from low-lying isomers. Again, these structures alone cannot account for the 2290 cm^{-1} band which is consistent with the N_2 stretch in ${}^3\text{Li}^+\text{N}^2(\text{ins.})$, ${}^3\text{Li}^+\text{N}^1\text{O}^1(\text{ins.})$ and ${}^3\text{Li}^+\text{O}^2(\text{ins.})$ inserted structures (see Figure 5b). We have not observed inserted structures in our previous studies of $\text{M}^+(\text{N}_2\text{O})_n$ complexes though it is possible that these bands have been obscured by stronger features.^[35,36] We cannot, however, exclude the possibility that this weak, blue-shifted band is an overtone or combination band. We performed anharmonic vibrational frequency calculations on the molecularly-bound and inserted isomers of $\text{Li}^+(\text{N}_2\text{O})_n$ ($n = 2,3$) and some combination bands do indeed lie close to the observed band at 2294 cm^{-1} . However, these bands are themselves calculated to be weak – less intense, in fact than the N_2 stretch in inserted structures. There thus remains some uncertainty regarding the interpretation of this feature.

Both Li^+ and N_2O are singlets in their ground state. LiO^+ has a triplet ground state, thus the O–atom transfer reaction is spin forbidden (and endothermic). One possible explanation is that the ${}^3\text{LiO}^+(\text{N}_2)$ complex is formed during the ablation process, which is then the seed for subsequent N_2O ligation.

As observed in Figure 2, as the number of ligands increases, the main band (molecularly N-bound ligands) smoothly red-shifts, an observation we ascribe to the proportionate reduction in σ -donation from each N-bound core ligand (see supporting material for relevant molecular orbitals). This red shift ceases at $n = 6$ which would be consistent with a complete coordination shell accordant with the DFT calculations. The IRPD spectra for $n = 7-9$ present a new band at 2228 cm^{-1} , very close to the free N_2O stretch, signifying weakly-bound ligands in a second, outer solvation shell.

3.2 $\text{Li}^+(\text{N}_2\text{O})_n\text{-N}_2$ IRPD Spectra

Given the above interpretation of inserted, $\text{OLi}^+\text{N}_2(\text{N}_2\text{O})$, structures in the spectra of $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2-4$) complexes, we performed a series of experiments replacing the Ar carrier gas with nitrogen. Figure 6 presents the IRPD spectra for the $\text{Li}^+(\text{N}_2\text{O})_n\text{-N}_2$ ($n = 2-8$) complexes. The spectra for complexes $n = 3-8$ show very similar band positions and relative band intensities to those of the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 3-8$) complexes (Figure 2). However, no discernible spectral features are observed in the IRPD spectrum for complex $n = 2$.

A direct comparison between the messenger moieties is presented in Figure 7. Figure 7a) presents the experimental IRPD spectra of $\text{Li}^+(\text{N}_2\text{O})_3\text{-N}_2$ along with $\text{Li}^+(\text{N}_2\text{O})_3\text{-Ar}$. The spectra are clearly very similar but both bands are somewhat broader in the N_2 -tagged spectra and the band separation is reduced slightly compared with the Ar-tagged complexes. Consistent with this, DFT calculations show slight changes in the vibrational modes when there is an Ar atom bound, or a N_2 ligand bound to the metal centre (see Supporting material).

Figure 7b) presents the experimental IRPD spectra of $\text{Li}^+(\text{N}_2\text{O})_2\text{-N}_2$ along with $\text{Li}^+(\text{N}_2\text{O})_2\text{-Ar}$. The lack of discernible bands in the $\text{Li}^+(\text{N}_2\text{O})_2\text{-N}_2$ spectrum indicates negligible photodissociation in this wavelength region implying that the N_2 is bound relatively strongly. Calculations support this interpretation - N_2 is calculated to be bound by 0.32 eV to the $^1\text{Li}^+\text{N}^2$, $^1\text{Li}^+\text{N}^1\text{O}^1$ and $^1\text{Li}^+\text{O}^2$ molecularly bound isomers, and by 0.31 and 0.27 eV to the inserted isomers ($^3\text{Li}^+\text{N}^1(\text{ins.})$ and $^3\text{Li}^+\text{O}^1(\text{ins.})$), respectively. This is significantly stronger than the calculated binding energy of the Ar atom, 0.14 eV for all isomers. Hence, any photon absorbed in this spectral region (*ca.* 0.28 eV) is comfortably

sufficient to lead to Ar loss but not necessarily N₂ loss. For the $n = 3$ complexes (Figure 7a) the N₂ moiety is bound to both the molecularly-bound and inserted isomers by 0.19 eV, whilst the Ar atom is bound by *ca.* 0.10 eV and so one-photon absorption brings about efficient tag loss in both cases.

Using nitrogen as the carrier gas, it was hoped that the N₂ would provide an infrared signature of its vibrational stretch, predicted around 2294 cm⁻¹ which would confirm the assignment of our bands in Figures 4 and 5. Instead, the N₂ is itself bound too strongly to the $n = 2$ complex and a further weakly-bound messenger (Ar) would be needed for efficient photodissociation. In the case of the $n = 3$ complexes, N₂ is weakly-bound and acts as a messenger itself. As a result, although the agreement with calculated band positions is good, we are unable to conclusively assign the 2294 / 2291 cm⁻¹ band as an N₂ stretch. One way to do this might be by employing a mass-selective technique which could observe photoinduced N₂ loss directly from [LiN_{2m}O_m]⁺ complexes.

3.3 Al⁺(N₂O)_{*n*}-Ar IRPD Spectra

Figure 8 presents the IRPD spectra for Al⁺(N₂O)_{*n*}-Ar complexes, $n = 2-6$. The spectra for complexes $n = 2, 3$ comprise a strong band at 2238 cm⁻¹ and 2237 cm⁻¹, plus a weaker band at 2251 cm⁻¹ and 2250 cm⁻¹, respectively. These bands become increasingly merged as the number of ligands increases. As with Li⁺N₂O the calculated potential energy surface for Al⁺N₂O supports two deep minima – a global Al⁺-NNO minimum and a secondary, slightly bent Al⁺-ONN well (see Figure 9a). Again, the two potential minima are very close to isoegetic (Figure 9b) but the broader O-bound minimum leads to the zero point energy here being lower than that in the deeper N-bound minimum. The barrier to internal rotation is, however, significantly lower in this case (~ 0.5 eV) than in the Li⁺(N₂O) complex (~ 0.8 eV) and the T-shaped intermediate structure is calculated to be relatively unbound.

Figure 10 shows the IRPD spectrum of [AlN₄O₂Ar]⁺ along with the simulated vibrational spectra of energetically low-lying molecularly-bound isomers. The energetic ordering of different structures makes a stark contrast with those of [LiN₄O₂Ar]⁺. For [AlN₄O₂Ar]⁺ we calculate the

inserted, ${}^1\text{Al}^+\text{N}^1(\text{ins.})$ and ${}^1\text{Al}^+\text{O}^1(\text{ins.})$, structures to be markedly lower in energy than the molecularly bound ${}^1\text{Al}^+\text{N}^2$, ${}^1\text{Al}^+\text{N}^1\text{O}^1$, ${}^1\text{Al}^+\text{O}^2$. The simulated spectra of the inserted isomers, however, agree poorly with the observed IRPD spectrum which is well-reproduced by the molecularly-bound structures. This implies a significant barrier to insertion which cannot be efficiently surmounted under our molecular beam conditions.

Different from any of the previous $\text{M}^+(\text{N}_2\text{O})_n$ complexes we have studied previously,[35,36] N- and O- bound ligands in $[\text{AlN}_4\text{O}_2\text{Ar}]^+$ are not spectrally distinguishable. Indeed, analysis of the predicted motion suggests the N_2O vibrations are highly coupled and less localised on individual ligands. In this sense, the ligand vibrations in the molecularly-bound $\text{Al}^+(\text{N}_2\text{O})_2$ isomers act very similarly to the CO_2 ligands in $\text{Al}^+(\text{CO}_2)_n$ observed by Duncan and coworkers.[58] In $\text{Al}^+(\text{CO}_2)_n$, non-linear structures were attributed to the sequential CO_2 binding at the $3s^2$ Al^+ centre. Briefly, the CO_2 ligands do not add to the metal centre according to VSEPR (for $n = 2$ we would expect a linear structure), but rather bind to the same side of the metal ion. Explained by Bauschlicher and coworkers to account for the structure of $\text{Mg}^+(\text{CO}_2)_2$ [59,60] and then by Duncan,[58] as the first CO_2 ligand binds to the cationic metal centre, it polarises the valence electron distribution inducing a negative charge on the opposite side of the metal ion. A second ligand avoids this negative charge by binding to the same side as the first ligand. The similarity of structures calculated here for $\text{Al}^+(\text{N}_2\text{O})_2$ isomers with those observed for $\text{Al}^+(\text{CO}_2)_n$, [58] suggests the same polarisation effect dominates.

The coupled N_2O ligand vibrations behave similarly to CO_2 ligands. For the $n = 2$ complex, both the in-phase and out-of-phase combinations of the two ligand ν_3 stretches must be considered. The observed spectrum presents two bands at 2238 and 2251 cm^{-1} , respectively. By considering the calculated motions of the N_2O ligands, the stronger band at 2238 cm^{-1} is assigned to the out-of-phase asymmetric (N=N) combination, with the 2251 cm^{-1} band assigned to the in-phase combination (with reduced dipole moment). The combinations are present in the simulated spectra of all three molecularly-bound isomers, ${}^1\text{Al}^+\text{N}^2$, ${}^1\text{Al}^+\text{N}^1\text{O}^1$ and ${}^1\text{Al}^+\text{O}^2$ and it seems likely that the observed IRPD spectrum comprises a mixture of all three.

As in the Li^+ complexes, σ -donation is inefficient and thus, the observed vibrational bands are only slightly blue-shifted from those in isolated N_2O . As n increases, the number of possible combinations of ligand stretches increases, leading to a broader spread of simulated stretches which is reflected in the spectral broadening of the IRPD bands as n increases.

4. Discussion

It is informative to plot the IRPD peak positions as a function of complex size, as illustrated in Figure 11. To extract the exact band positions, the observed spectra were fit to sums of Gaussian functions. The peak positions in the $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$ series show little variation with increasing complex size and the band merely broadens and the band centre blue-shifts slightly. From the calculated structures, as the ligand number increases beyond $n = 2$, the inner two ligands approach the Al^+ centre more closely, leading to more 7σ donation and a slightly enhanced blue-shift.

The peak positions in the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ series can be more clearly assigned as arising from N- and O-bound ligands and inserted structures. The weaker, highest frequency band ($n = 2\text{--}6$) is tentatively assigned as an N_2 stretch in inserted, $\text{OLi}^+\text{N}_2(\text{N}_2\text{O})_{n-1}$, isomers. The main, stronger band in the spectra of all complex sizes is due to molecularly-bound N- or O-bound N_2O ligands. Confirmed from DFT calculations, the coordination number for the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ series is six, explaining the discontinuity in the trend in frequency with $n = 6$. The new band which appears *ca.* 2228 cm^{-1} for $n > 6$ arises from weakly-bound N_2O ligands in an outer coordination shell.

Li^+ and Al^+ metal centres were chosen to determine the effect of the closed-shell s^2 configuration ion on the structures generated and how they might differ from other metal centres studied previously (d^{10} coinage metal ions and group 9 monocations).[35,36] The differences are marked. Firstly, molecularly N- and O-bound ligands are almost spectrally indistinguishable. Secondly, in the case of $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$ complexes, the N_2O ligand vibrations are no longer local modes and act collectively in a similar way to CO_2 ligands yielding IRPD spectra which are similar

for each complex, and broaden as the complex size increases. In the case of group 9 and 11 cations σ donation from the N_2O 7σ orbital into partially-filled $s-d_z^2$ on the metal ion leads to significant stabilisation of the N-bound ligands relative to O-bound equivalents. In the case of the present $1s^2$ ($3s^2$) configuration ions, s-d hybridisation is not energetically feasible and the two binding motifs are effectively isoenergetic and spectrally indistinguishable at this level. Previous investigations on the interactions of group 13 cations with rare-gases also concluded no significant s-d hybridisation, consistent with this study.[61-63] The blue shift of N-bound ligands for $n = 2$ is less pronounced in Al^+ complexes than for Li^+ reflecting the weaker electrostatic interactions of the larger ion.

Despite lying much higher in energy than molecularly-bound ligands, the spectra for the $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ complexes exhibit some evidence of an N_2 stretch indicating metal ion insertion into the N_2O molecule. This band is blue-shifted from the molecularly-bound ligands, N- and O-bound isomers of which are spectrally overlapped. By contrast, in the case of $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$, the inserted structures are calculated to be clearly the lowest in energy and yet the experimental spectra show little evidence for them. Instead the spectra are well-reproduced by molecularly-bound complexes.

5. Conclusions

The structures of gas-phase $\text{M}^+(\text{N}_2\text{O})_n$ complexes ($\text{M} = \text{Li}, \text{Al}$) have been studied using a combination of IRPD action spectroscopy and density functional theory. Spectral simulations based on calculated molecularly-bound structures show little energetic or spectral difference between the N- and O-bound ligands. However, large barriers to internal rotation are predicted to result in trapping of both N- and O-bound ligands leading to a wide range of potential isomers. The spectral widths observed for the larger complexes are consistent with this picture.

Uniquely amongst the $\text{M}^+(\text{N}_2\text{O})_n$ complexes we have studied, the IRPD spectra of the $\text{Li}^+(\text{N}_2\text{O})_n$ complexes ($n = 2\text{--}6$) show some evidence of an N_2 moiety, which we tentatively assign as arising from inserted, $\text{OLi}^+\text{N}_2(\text{N}_2\text{O})_{n-1}$ isomers. The N_2 band arising from this moiety is spectrally distinct and

blue-shifted from the molecularly-bound N- and O-bound ligands and is well reproduced when compared to simulated spectra calculated using density functional theory. In the case of $\text{Al}^+(\text{N}_2\text{O})_n$ complexes there is no evidence of inserted $\text{OAl}^+\text{N}_2(\text{N}_2\text{O})_{n-1}$ isomers as the N_2 band, which is also predicted to be blue-shifted, does not agree with the experimental spectra. The experimental spectra are however well represented by molecularly-bound N_2O ligands.

Disclosure statement

There are no conflicts to declare.

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Statement of Article Significance

This manuscript forms part of an ongoing series of infrared studies of $\text{M}^+(\text{N}_2\text{O})_n$ species as entrance-channel complexes for the metal-centred nitrous oxide reduction reaction. $\text{M}^+ = \text{Li}^+$ and Al^+ are closed *s*-shell ions which make for interesting comparison with previous work on coinage metal (d^{10}) and group 9 metal ion complexes revealing periodic trends in the structures of these complexes with different ions. In the complexes studied here, unlike in other systems, there is little evidence of spectrally distinct N- and O-bound ligands but some tentative evidence of inserted structures.

Figures

Figure 1. Time-of-flight mass spectrum of $\text{Li}^+(\text{N}_2\text{O})_n$ and $\text{Al}^+(\text{N}_2\text{O})_n$ complexes produced by ablation of a Li/Al (1:9) alloy target in an argon carrier gas seeded with 0.6% N_2O . $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ peaks are indicated by arrows with $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$ complexes also being formed (*).

Figure 2. Experimental IRPD spectra of $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2 - 9$) complexes in the region of the N_2O asymmetric (N=N) stretch. In each case depletion of the ion signal occurs due to the loss of the Ar messenger atom. For comparison the depletion intensity for each complex size was normalized with the maximum value in this region. The vertical dashed line indicates the wavenumber of the $\nu_3(\text{N}=\text{N})$ mode in isolated N_2O at 2223.5 cm^{-1} .^[53]

Figure 3. (a) Calculated potential energy surface for the $\text{Li}^+\text{N}_2\text{O}$ complex showing a linear Li^+NNO global minimum structure and a deep quasilinear Li^+ONN minimum. This PES was generated by fixing the N_2O molecule at its equilibrium geometry. (b) Minimum-energy pathway as a function of bond angle illustrating the relative energies of N- and O-bound minima. For this PES the N_2O geometry was allowed to relax at each step. Horizontal lines indicate the energy of the respective geometry-optimised structures including zero point correction.

Figure 4. Experimental IRPD spectrum of $[\text{LiN}_4\text{O}_2\text{Ar}]^+$ in the region of the N_2O asymmetric ($\text{N}=\text{N}$) stretch along with simulated vibrational spectra of energetically low-lying isomers. Simulated IR bands corresponding to N-bound and O-bound ligands, and $\text{N}\equiv\text{N}$ vibrations in insertion structures are indicated in blue, red and green respectively. The relative energies of the different calculated isomers are given in eV. The vertical dashed lines at 2223.5 cm^{-1} and 2330 cm^{-1} indicate the wavenumber of the ν_3 ($\text{N}=\text{N}$) mode in isolated N_2O and isolated N_2 , respectively.[53]

Figure 5. Experimental IRPD spectra of $[\text{LiN}_6\text{O}_3\text{Ar}]^+$ along with a) simulated vibrational spectra of energetically low-lying isomers of the ground state singlet state and b) simulated vibrational spectra of insertion isomers in the triplet state in the region of the N_2O asymmetric ($\text{N}=\text{N}$) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. The relative energies of the different isomers are given in eV. The vertical dashed lines at 2223.5 cm^{-1} and 2330 cm^{-1} indicate the wavenumber of the ν_3 ($\text{N}=\text{N}$) mode in isolated N_2O and isolated N_2 , respectively.[53]

Figure 6. Experimental IRPD spectra of $\text{Li}^+(\text{N}_2\text{O})_n\text{-N}_2$ ($n = 2 - 8$) complexes in the region of the (N=N) stretch in N_2O and in N_2 . For ease of comparison the spectra for $n \geq 3$ have been normalized. The vertical dashed lines at 2223.5 cm^{-1} and 2330 cm^{-1} indicate the wavenumber of the ν_3 (N=N) mode in isolated N_2O and isolated N_2 , respectively.[53]

Figure 7. Experimental IRPD spectra of a) $\text{Li}^+(\text{N}_2\text{O})_3\text{-N}_2$, $\text{Li}^+(\text{N}_2\text{O})_3\text{-Ar}$ and b) $\text{Li}^+(\text{N}_2\text{O})_2\text{-N}_2$, $\text{Li}^+(\text{N}_2\text{O})_2\text{-Ar}$ complexes in the region of the N_2O asymmetric (N=N) stretch. In each case depletion of the ion signal occurs due to either the loss of the N_2 messenger molecule or the loss of the Ar messenger atom. For comparison the depletion intensity for each complex size has been approximately normalized with the maximum value in this region. The vertical dashed lines at 2223.5 cm^{-1} and 2330 cm^{-1} indicate the wavenumber of the ν_3 (N=N) mode in isolated N_2O and isolated N_2 , respectively.[53]

Figure 8. Experimental IRPD spectra of $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2 - 6$) complexes in the region of the N_2O asymmetric (N=N) stretch. In each case depletion of the ion signal occurs due to the loss of the Ar messenger atom. For comparison the depletion intensity for each complex size was normalized with the maximum value in this region. The vertical dashed line indicates the wavenumber of the $\nu_3(\text{N}=\text{N})$ mode in isolated N_2O at 2223.5 cm^{-1} .^[53]

Figure 9. (a) PES for the $\text{Al}^+\text{N}_2\text{O}$ complex showing a linear, ground-state minimum, $\text{Al}^+\text{--NNO}$ and a secondary non-linear minimum, $\text{Al}^+\text{--ONN}$. This PES was generated by fixing the N_2O molecule at its equilibrium geometry. (b) Minimum-energy pathway as a function of bond angle illustrating the relative energies of N- and O-bound minima. For this PES the N_2O geometry was allowed to relax. Horizontal lines indicate the energy of the respective geometry-optimised structures including zero point correction.

Figure 10. Experimental IRPD spectra of $[\text{AlN}_4\text{O}_2\text{Ar}]^+$, along with simulated vibrational spectra of energetically low-lying molecularly-bound and inserted isomers of the ground singlet state in the region of the N_2O asymmetric ($\text{N}=\text{N}$) stretch. Simulated IR bands corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively. Simulated IR bands corresponding to the N_2 moiety are indicated by an asterisk (*). The relative energies of the different isomers are given in eV. The vertical dashed lines at 2223.5 cm^{-1} and 2330 cm^{-1} indicate the wavenumber of the ν_3 ($\text{N}=\text{N}$) mode in isolated N_2O and isolated N_2 , respectively.[53]

Figure 11. Experimental resolved peak positions displayed as a function of cluster size for $\text{Li}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2-9$) and $\text{Al}^+(\text{N}_2\text{O})_n\text{-Ar}$ ($n = 2-6$) complexes. The size of each point represents the intensity relative to the maximum band in each complex size. Uncertainties correspond to the full-width-half-maximum (FWHM) of fitted Gaussian functions used to determine the exact position of each band. The horizontal dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1} .^[53]

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