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1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas^{1,2} accounting for around 5% of anthropogenic emissions and has a warming potential almost 300 times greater than carbon dioxide.³ As a result, there is considerable interest in reducing N₂O emissions, especially from automobile combustion engines. To this end, modern vehicles employ metal-catalysed nitrogen oxide reduction in their three-way catalytic converters.^{4,5} The transition metals used are usually found in a highly dispersed form such as nanoparticles and the study of small isolated metal clusters is thus a vibrant and active research area.⁶ Understanding the physical and chemical properties of transition metal clusters has wider importance in the fields of heterogeneous catalysis, solid-state physics, surface chemistry, and organometallic chemistry.⁷⁻¹¹ In this context, gas-phase metal clusters represent tractable model systems for developing molecular level insight into the thermodynamics and kinetics of catalytic reactions. Decades of work have shown that this activity depends on a complex interplay of various factors,

Infrared action spectroscopy of nitrous oxide on cationic gold and cobalt clusters†

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Understanding the catalytic decomposition of nitrous oxide on finely divided transition metals is an important environmental issue. In this study, we present the results of a combined infrared action spectroscopy and quantum chemical investigation of molecular N₂O binding to isolated Au_n⁺ ($n \le 7$) and Co_n⁺ ($n \le 5$) clusters. Infrared multiple-photon dissociation spectra have been recorded in the regions of both the N=O (1000–1400 cm⁻¹) and N=N (2100–2450 cm⁻¹) stretching modes of nitrous oxide. In the case of Au_n⁺ clusters only the ground electronic state plays a role, while the involvement of energetically low-lying excited states in binding to the Co_n⁺ clusters cannot be ruled out. There is a clear preference for N-binding to clusters of both metals but some O-bound isomers are observed in the case of smaller Co_n(N₂O)⁺ clusters.

including size, geometry, local charge density, dimensionality, electronic structure, and the presence as well as properties of defect sites.^{12–21}

Many experimental studies have investigated the structural evolution of isolated gold clusters with atom number.²²⁻²⁴ Early investigations utilised ion mobility mass spectrometry, which, combined with quantum chemical calculations, is a powerful tool for structure determination of charged metal clusters.²⁵ Kappes and coworkers have performed such studies on charged gold clusters up to $n = 14^{26,27}$ and determined planar groundstate structures for Au_n^+ (n = 3-7) and Au_n^- (n = 3-11), respectively. Anionic gold clusters were investigated further by electron diffraction confirming these structural motifs, revealing a possible chiral structure for Au₃₄^{-.28,29} Building on previous spectroscopic studies of Au_n^+ ($n \le 5$) clusters, 30-33Ferrari et al. have recently reported far-infrared multiple photon dissociation spectroscopy (IR-MPD) studies of Au_n^+ $(n \le 9)$, identifying both 3D and planar isomers for $n = 8.^{34}$ IR-MPD studies have also been performed on neutral gold clusters up to 20 gold atoms, revealing two-dimensional, planar structures up to Au₁₀, with the onset of 3D structures for Au₁₁ at 100 K.^{35–37} At room temperature, however, planar and non-planar isomers coexist for Au₈, Au₉, and Au₁₀. The largest cluster studied, Au₂₀, was shown to have a pyramidal structure.³⁸

Reactions between cationic gold clusters, Au_n^+ (n = 1-4), and N₂O have been studied by Dietrich *et al.* combining a Penning trap with time-of-flight (ToF) mass spectrometry.³⁹ Dissociative charge transfer yielding Au_nN and NO⁺ was the major reaction channel for n = 1 and 2, but a range of other products, including

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Au_nO⁺, Au_nN⁺ and Au_nNO⁺, were also detected, with n = 1 and 3 clusters leading preferentially to N==O bond rupture and the n = 2 cluster breaking the N==N bond. Relevant structural information on nitrogen oxides adsorbed to gold clusters is limited to the IR-MPD study of Au_n(NO)⁺ by Fielicke and coworkers.⁴⁰ Marked nitric oxide activation was observed in binding to the odd-electron, even-*n*, Au_n⁺ clusters, reflecting efficient unpaired electron donation into the NO π^* orbital. NO was found to bind non-linearly in atop arrangements, tending to favour low-coordinated gold atoms.

Gehrke *et al.* have employed IR-MPD to identify the structures of Co_n^+ -Ar (n = 4-8) clusters.⁴¹ All clusters observed exhibit high spin states and significant Jahn–Teller distortion and, unusually, the vibrational spectra of Co_n^+ were shown to be strongly dependent on the number of adsorbed Ar messenger atoms. More recently, an IR-MPD study by Jia *et al.* on Co_n^+ -Ar_m (n = 3-5, m = 3, 4) confirmed these structural findings,⁴² and the high spin states of isolated Co_n^+ (n = 4-9)clusters have been measured by X-ray absorption and X-ray magnetic circular dichroism spectroscopy.⁴³ The structures of neutral Co_n clusters (n = 4-10, 13) have also been studied using two-colour IR-UV spectroscopy.⁴⁴

Reactions of Co_n^+ (n = 4-30) clusters with NO and N₂O have been investigated using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry under single-collision conditions.⁴⁵ Reactions with N₂O typically proceed much more slowly than the collision rate and result in the formation of simple cluster oxides, $\text{Co}_n \text{O}_m^+$. By contrast, NO chemisorption rates exceed calculated collision rates. In both reactions there is evidence for cluster fragmentation, characterised typically by Co atom evaporation, and multiple collisions result in N₂O decomposition leading to N₂ loss. No molecularly adsorbed, *i.e.* $\text{Co}_n(\text{N}_2\text{O})^+$, clusters were observed under single-collision conditions.

Theoretical studies by Castro and coworkers, utilising density functional theory methods, investigated the catalytic N₂O reduction by Rh₆⁻ and Rh₆⁺ clusters⁴⁶ as well as the low-symmetry Pt₈ cluster.⁴⁷ We have previously reported IR-MPD studies of N₂O binding on Rh_n⁺ (n = 4-8)⁴⁸⁻⁵⁰ and Pt_n⁺ clusters (n = 1-8).⁵¹ Extensive IR-induced reactivity was observed in both cases, with excitation of infrared modes resulting in N₂O decomposition. By way of comparison with these studies, we report here an IR-MPD study of N₂O adsorption on isolated Au_n⁺ ($n \le 7$) and Co_n⁺ ($n \le 5$) clusters in which we investigate the nature of the molecular binding and its dependence on cluster size, electronic and geometrical structure.

2. Experimental and computational methodology

The instrument at the Fritz-Haber Institute along with the infrared multiple photon dissociation (IR-MPD) technique employed have been described previously and only brief details are given here.^{52,53} Gas-phase $M_n(N_2O)^+$ (M = Co, Au) clusters are formed by entraining metal atoms/ions produced by pulsed

laser ablation of a rotating metal rod within an intense pulse of helium carrier gas (10 bar backing pressure), with nitrous oxide introduced downstream *via* a late mixing valve. Efficient clustering and thermalisation occurs *via* collisions within an aggregation channel before expansion into vacuum creating the molecular beam. The beam is skimmed for collimation and positively-charged clusters are detected by orthogonal extraction into a reflectron time-of-flight mass spectrometer.⁵⁴ Experimental parameters such as the total backing pressure behind the pulsed valve, ablation laser power and nitrous oxide partial pressure are optimised for the generation of $M_n(N_2O)^+$ (M = Co, Au; $n \le 8$) species of interest. For these experiments the source was operated at room temperature and the cluster distribution is assumed to be in thermal equilibrium with this.

Intense tunable pulsed infrared radiation is provided by the free electron laser (FEL) at the Fritz-Haber Institute (FHI),⁵³ operating in the regions of 1000–1400 cm⁻¹ and 2100–2450 cm⁻¹ and covering the ν_1 (N=O) and ν_3 (N=N) stretching modes of N₂O, respectively.⁵⁵ The IR beam is collinear with and counterpropagates the molecular beam, and IR-MPD spectra are recorded by monitoring the loss of N₂O from the parent M_n(N₂O)⁺ cluster as a function of wavenumber.^{56–62} In this way, photofragmentation provides a signature of IR absorption. To account for photon flux fluctuations, all experimental spectra were corrected for laser power.

To interpret the experimental vibrational spectra, quantum chemical calculations were performed, yielding structures and simulated infrared spectra of energetically low-lying isomers. Density functional theory (DFT) calculations were performed using the hybrid meta-GGA functional TPSSh, which includes 10% exact Hartree-Fock exchange,63 together with the Def2-TZVP basis set, a combination which has worked well in previous studies.^{64,65} Relativistic effects, essential in describing gold chemistry,66-68 were incorporated by means of the ECP-60 effective core potential (ECP)⁶⁹ for all but the 19 valence electrons of each gold atom. Def2-TZVP was also shown to accurately predict the IR spectra of $Rh_n(CO)_m^+$ clusters.⁷⁰ The quadratically convergent SCF procedure was used along with 1.00×10^{-6} hartree convergence criterion along with the Gaussian 09 "very tight" geometry optimisation convergence.⁷¹ Plausible N₂O binding at atop, bridge, and three-body binding sites were investigated with N2O found to bind exclusively atop, favouring low coordinated gold/cobalt atoms, with μ_2 and μ_3 arrangements converging to atop structures upon geometry optimisation. The lowest energy structures found typically involve dissociatively-adsorbed nitrous oxide, with molecularly-bound structures representing entrance-channel complexes trapped behind an activation barrier. There is no evidence for dissociative structures in the experimental spectra; N₂ almost certainly desorbs as a result of the exoergicity of the dissociation and subsequent O-atom binding. To better compare with experimental spectra, all simulated IR spectra reported here have been scaled by a factor 0.955, determined from the simulated vibrational wavenumbers of isolated N2O.55 All calculations were performed using the Gaussian09 suite of programs,⁷¹ and relative energies of structural isomers are given in electron



Fig. 1 (a and b) Time-of-flight mass spectrum of Au_n^+ clusters produced by laser ablation of a gold rod in the presence of a helium carrier gas (10 bar backing pressure) and N₂O added downstream in the cluster channel.

volts (eV), inclusive of zero-point energy. To accurately determine the multiplicity of each cluster structure, together with the relative energy, for each calculated structure the DFT wavefunction was stabilised and tested.

3. Results and discussion

3.1 $Au_n(N_2O)^+$ clusters

Fig. 1 presents the ToF mass spectrum showing the production of Au_n^+ (n = 1-8) clusters along with attached adsorbates. Besides the naked Au_n^+ cluster cations, the most intense signals in the spectrum are the target $Au_n(N_2O)^+$ clusters as well as additional peaks attributable to the simple cluster oxides, $Au_nO_m^+$ and, uniquely in the case of n = 1, $AuO(N_2O)^+$. Other species are observed, which we believe arise from reactions with trace hydrocarbons in the source, possibly introduced by glue used for sticking the rod to the holder. For the smallest, n = 1 and 2 clusters, the species produced here are different to those observed by Dietrich *et al.* in their single-collision



Fig. 2 IR-MPD depletion spectra of Au_n(N₂O)⁺ (n = 3-7) clusters with depletion given as a percentage of ion signal. The vertical dashed lines at 1285 and 2224 cm⁻¹ indicate the wavenumber of the ν_1 (N=O) and ν_3 (N=N) modes in isolated N₂O, respectively.⁵⁵

reaction study, reflecting the stabilising effect of collisions in the source employed here and the possible effects of fragmentation of larger clusters.

Fig. 2 shows an overview of the IR-MPD spectra for $Au_n(N_2O)^+$ (n = 3-7) species recorded in the spectral region of both the N=O (1000–1400 cm⁻¹) and N=N (2100–2450 cm⁻¹) stretches and presented as depletion in the parent ion signal. The presence of intense depletion bands (in some cases exceeding 60% of the parent ion signal) close to the vibrational bands in free nitrous oxide confirms the molecular nature of the N₂O binding. In this respect, $Au_n(N_2O)^+$ clusters are similar to the isoelectronic $Au_n(OCS)^+$ species whose spectra we have reported recently.⁷² The spectra of the n = 1 and 2 species unfortunately suffer from substantial distortions arising from dissociation of larger species (see Fig. S4 and S5, ESI†).

In Fig. 2, a single band is observed in the N=O stretch region around 1340 cm⁻¹, blue-shifted up to 60 cm⁻¹ from the ν_1 mode of free N₂O at 1285 cm⁻¹.⁵⁵ The blue-shift reduces smoothly with increasing cluster size from 1345 cm⁻¹ for n = 3, to 1334 cm⁻¹ for n = 7. A similar trend is observed in the N=N stretch region as the main band moves from 2278 cm⁻¹ for n = 3 to 2266 cm⁻¹ for n = 7, again slightly blue-shifted from the ν_3 mode of N₂O at 2224 cm⁻¹.⁵⁵ In the latter spectral region a weak shoulder to the main spectral feature is observed for



Fig. 3 IR-MPD spectrum of Au₃(N₂O)⁺, along with simulated IR spectra of energetically low-lying isomers. The only low-lying electronic state is a singlet state and simulated IR bands corresponding to N-bound and O-bound isomers are indicated in blue and red, respectively. Energies are given in eV relative to the lowest molecularly bound isomer. The vertical dashed lines at 1285 and 2224 cm⁻¹ indicate the wavenumber of the ν_1 (N=O) and ν_3 (N=N) modes in isolated N₂O, respectively.⁵⁵

clusters n = 3 and 4, close to the free N₂O stretch which is not present for the larger species.

Interpretation of the IR-MPD spectra is greatly assisted by simulated infrared spectra of energetically low-lying isomers identified using DFT. By way of example, the observed spectra of $Au_3(N_2O)^+$ and $Au_4(N_2O)^+$ are presented in Fig. 3 and 4, respectively, along with simulated spectra of low-lying structural isomers.

For $Au_3(N_2O)^+$ (Fig. 3), the observed spectrum agrees very well with the simulated spectrum of the N-bound, lowest energy molecularly-bound structure with both spectral features blueshifted from the free N₂O bands. With fractional depletion of >50% observed, it is clear that this structure dominates the distribution. It is tempting to interpret the shoulder at 2223 cm⁻¹ as the higher energy O-bound isomer but there is little evidence for the equivalent red-shifted band in the N=O stretch region. By contrast, both N- and O-bound isomers were observed in our recent study of $Au(N_2O)_x^{+,73}$ The origin of this shoulder remains unclear but could represent the presence of another N-bound isomer. Alternatively, it could result from spectral power broadening due to the increased FEL power in the N=N stretching region and the fact that fewer higher energy photons are required for IR-MPD in this region.

In the case of $Au_4(N_2O)^+$ (Fig. 4), a richer distribution of lowlying structural isomers is predicted. However, it is clear that the vibrational spectrum in this region is diagnostic only of the nitrous oxide binding motif and not of the metal cluster



Fig. 4 IR-MPD depletion spectrum of Au₄(N₂O)⁺, along with simulated IR spectra of low-lying isomers in the region of the N₂O N=O and N=N stretches. The low-lying structures have doublet multiplicity. Simulated IR bands corresponding to N-bound and O-bound isomers are indicated in blue and red, respectively, with relative energies given in eV. The vertical dashed lines at 1285 and 2224 cm⁻¹ indicate the wavenumber of the ν_1 (N=O) and ν_3 (N=N) modes in isolated N₂O, respectively.⁵⁵

structure. Again, the spectrum is dominated by N-bound structures with limited evidence for O-binding.

In both spectral regions, the weak blue shift observed in the N-bound isomers relative to the free N₂O stretches can be explained by σ -donation from the 7σ (HOMO-1) orbital in N₂O to the metal cluster, which is antibonding with respect to the N=N bond. By contrast, O-binding, if present, would be signified by negligible shifts in the N=N stretch region but a marked red shift in the N=O band, reflecting an increased effective reduced mass. The nature of N₂O binding to metal centres has been discussed extensively previously.^{4,73-75}

The above interpretation of $Au_n(N_2O)^+$ binding is readily extended to the larger, n = 5-7 clusters, in which single blue-shifted bands in both spectral regions are again assigned to N-bound isomers.

3.2 $Co_n(N_2O)^+$ clusters

Fig. 5 shows the ToF mass spectrum of Co_n^+ -based clusters generated, exhibiting the production of $\text{Co}_n(\text{N}_2\text{O})^+$ species as far



Fig. 5 (a and b) Mass spectrum of ions observed following ablation of a cobalt rod along with N₂O added downstream in the cluster channel. For clarity, the mass signal for $Co_2(N_2O)_2^+$ is marked with an asterisk (*). (c) Histogram showing relative abundance of major species observed relative to the naked Co_n^+ mass signal. The larger clusters react readily with N₂O forming simple oxides.

as n = 5. Considerably more $\text{Co}_n \text{O}_m^+$ (m = 1-4) oxidation products are observed than for the gold clusters (see Fig. 5c).



Fig. 6 IR-MPD depletion spectra of $\text{Co}_n(\text{N}_2\text{O})^+$ (n = 1-5) clusters in the N=O and N=N regions of N₂O. The vertical dashed lines at 1285 and 2224 cm⁻¹ indicate the wavenumber of the $\nu_1(\text{N=O})$ and $\nu_3(\text{N=N})$ modes in isolated N₂O, respectively.⁵⁵

However, care needs to be taken in ascribing these to reactions with particular Co_n^+ clusters. Under single-collision conditions, the $\text{Co}_n^+ + \text{N}_2\text{O}$ reaction has previously been shown to result in efficient fragmentation of metal clusters in this size regime, notably as $\text{Co}_n^+ + \text{N}_2\text{O} \rightarrow \text{Co}_{n-1}\text{O}^+ + [\text{Co},\text{N}_2]$.⁴⁵ Hence, the observation of species such as Co_5O_4^+ almost certainly reflects reactions of larger clusters as well as Co_5^- itself.

Despite the abundance of oxides observed, sufficient $\text{Co}_n(\text{N}_2\text{O})^+$ signals were produced to permit IR-MPD spectra of $\text{Co}_n(\text{N}_2\text{O})^+$ clusters (n = 1-5) to be recorded, as shown in Fig. 6. The spectra of the very smallest (n = 1, 2) species again suffer enhancements (observed as negative depletions) due to fragmentation of larger and/or multiply decorated clusters, especially $\text{Co}_n(\text{N}_2\text{O})_2^+$, at the same wavenumber. Nevertheless, the observation of multiple spectral features in this region, including peaks red-shifted from the free N₂O band, signifies the presence of both O-bound and N-bound N₂O cluster structures.

A mix of N- and O-bound isomers was observed in related IR spectra of $\text{Co}(N_2\text{O})_x^+$ complexes in which the barrier for $N_2\text{O}$ free internal rotation in the $\text{Co}(N_2\text{O})^+$ complex was calculated to be *ca.* 1.3 eV (0.8 eV from the O-bound minimum).⁷⁶ Given the rate of collisions in the cluster formation channel, it is thus likely that a fraction of complexes become trapped in low-lying excited isomeric forms behind barriers of this magnitude.

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Fig. 7 IR-MPD depletion spectrum of $Co_3(N_2O)^+$, along with simulated IR spectra of low-lying isomers. Simulated IR spectra corresponding to N-bound and O-bound ligands are indicated in blue and red, respectively, for the two lowest energy calculated electronic states. The relative energies to the lowest molecularly bound isomer are given in eV. The vertical dashed lines at 1285 and 2224 cm⁻¹ indicate the wavenumber of the $\nu_1(N=O)$ and $\nu_3(N=N)$ modes in isolated N₂O, respectively.

The larger clusters, however, represent more effective thermal heat baths facilitating a more efficient annealing of structures. Hence, the spectra of the larger n species are dominated by the lower energy N-bound isomers.

The strongest feature in the N=O stretch region (ranging from 1345 cm⁻¹ for n = 1 to 1323 cm⁻¹ for n = 5) is characteristic of an N-bound structure. For n = 5 this band exceeds 80% depletion suggesting this is the dominant structure present. The lower fractional depletions observed for smaller cluster sizes reflect the presence of other isomers in the beam. In the N=N stretch region, by contrast, all spectra exhibit one main band slightly blue-shifted from the ν_3 band of N₂O with a shoulder observed very close to the free ν_3 stretch. Similarly to the N=O region, the main band is slightly more strongly blue-shifted for the smallest cluster, n = 1, at 2280 cm⁻¹ compared with 2271 cm⁻¹ for n = 5.

Fig. 7 compares the IR-MPD spectrum of $\text{Co}_3(\text{N}_2\text{O})^+$ together with simulated spectra for low-lying calculated triplet (lowest energy) and quintet (1st excited state) isomeric forms, confirming the assignments above. The strong bands at 1337 cm⁻¹ and 2275 cm⁻¹, each blue-shifted from the free N₂O bands, are readily assigned as N-bound structures (most likely the lowest-lying triplet state; IR-MPD is comparatively insensitive to cluster electronic state). The broad feature at 1219 cm⁻¹ and the shoulder near 2220 cm⁻¹, by contrast, agree well with simulated bands of the triplet O-bound isomer.





Fig. 8 Relative energies of lowest energy molecularly-bound N- (shown in blue) and O-bound isomers (red) for (a) $Co_n(N_2O)^+$ and (b) $Au_n(N_2O)^+$ (n = 1-5).

In addition to multiple isomers, $\text{Co}_n(\text{N}_2\text{O})^+$ clusters with n = 4 and 5 are predicted to have several more low-lying electronic states, each with qualitatively similar IR spectra in this region (see ESI[†]).

The relative energies of the lowest N- and O-bound isomers of $M_n(N_2O)^+$ (M = Co, Au; n = 1-5), are shown in Fig. 8 for the lowest energy electronic state in each case. For all cluster sizes, the N-bound isomers (blue) represent the lowest energy molecularly-bound structures, however the relative energies of the higher-lying O-bound structures (red) vary with cluster size, especially in the case of cobalt clusters.

In the case of $Au_n(N_2O)^+$, the energy difference between N- and O-bound isomers reduces smoothly with cluster size between n = 1 (0.45 eV) and n = 5 (0.35 eV). For the $Co_n(N_2O)^+$ clusters the picture is more complicated. Many more low-lying electronic states exist for the $Co_n(N_2O)^+$ clusters (see ESI†), especially for the even n, odd electron clusters for which doublet, quartet and sextet states all lie within 1.3 eV of the lowest energy structures. $Co_2(N_2O)^+$ has an anomalously low-lying O-bound state (*ca.* 0.24 eV in both doublet and sextet states). We have not calculated the barrier to internal N₂O rotation for each cluster (which interchanges N- and O-bound isomers) but evidence of O-bound structures in the spectra of $Co_n(N_2O)^+$ clusters suggests a significant barrier behind which the higher energy structures can be trapped. As discussed



Fig. 9 Relative ligand binding energies (given as absolute values) of lowest energy molecularly-bound N- and O-bound isomers for (a) $Co_n(N_2O)^+$ (n = 1-5), and (b) $Au_n(N_2O)^+$ (n = 1-5), calculated as $E[M_n(N_2O)^+] - E[M_n^+] - E[N_2O]$, including zero-point correction.

above, such structures have been observed in the spectra of $M(N_2O)_m^+$ for several individual metal ions^{73,76,77} but IR-MPD studies of $Rh_n(N_2O)^+$ and, recently, $Pt_n(N_2O)^+$ (n > 2) clusters concluded that N_2O binds exclusively *via* the terminal N-atom.^{48,49,51} This suggests that, as well as larger metal clusters providing better annealing, the barriers to N_2O rotation on Co_n^+ are unusually large.

The calculated ligand binding energies of the lowest energy molecularly-bound N- and O-bound isomers for $\text{Co}_n(\text{N}_2\text{O})^+$ and $\text{Au}_n(\text{N}_2\text{O})^+$ (n = 1-5) are presented in Fig. 9 illustrating the higher binding energy of N-bound structures relative to O-bound. The overall trend is for weaker binding with increased cluster size on both metals, though the N-bound isomer of $\text{Co}_2(\text{N}_2\text{O})^+$ is anomalously weakly bound.

4. Conclusions

The binding of nitrous oxide to small gas-phase Au_n^+ and Co_n^+ clusters has been investigated using IR-MPD spectroscopy in conjunction with density functional theory calculations of energetically low-lying molecularly bound structures. In the case of $Au_n(N_2O)^+$, the lowest energy N-bound isomers dominate the observed spectra as indicated by the slight blue-shift of vibrational bands relative to free N₂O. For $Co_n(N_2O)^+$, a richer

distribution of structural isomers is observed with clear evidence of both N- and O-bound isomers in the distributions produced for the smaller clusters. Calculations suggest the presence of more low-lying electronic states in the case of Co_n^+ but these are imperceptible in the vibrational spectra. In all cases investigated here, the only significant dissociation channel observed is the simple N₂O ligand loss with little or no clear evidence for the type of photoinitiated intra-complex reactivity previously characterised in the case of analogous $\text{Rh}_n(\text{N}_2\text{O})^+$ and $\text{Pt}_n(\text{N}_2\text{O})^+$ clusters^{48–51} and, more widely, in $\text{Au}_n(\text{OCS})^+$ and $\text{Pt}_n(\text{CO})^+$.^{72,78} This suggests that the transition states for the N₂O decomposition reaction on Co_n^+ and Au_n^+ lie significantly higher in energy than the $\text{M}_n^+ + \text{N}_2\text{O}$ dissociation asymptote.

Statement of author contributions

This work was conceived of by SRM, OD and AF and funded under their Oxford-Berlin Research Partnership grant designed to establish new collaborations between Oxford and Berlin. WS is responsible for the free electron laser at the Fritz-Haber Institute where all experiments were run. EMC, AEG, GM, PWB, and ASG visited Berlin for the experimental runs at which SS, KMP, KS and MF were also present. The computational studies were performed by EMC, AEG, GM and PWB. The manuscript was written in Oxford with contributions from all authors.

Conflicts of interest

There are no conflicts of interest to declare.

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