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Infrared spectra and fragmentation dynamics of isotopologue-selective mixed-ligand complexes†

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Isolated mixed-ligand complexes provide tractable model systems in which to study competitive and cooperative binding effects as well as controlled energy flow. Here, we report spectroscopic and isotopologue-selective infrared photofragmentation dynamics of mixed gas-phase $\text{Au}^{(12/13}\text{CO})_n(\text{N}_2\text{O})_m^+$ complexes. The rich infrared action spectra, which are reproduced well using simulations of calculated lowest energy structures, clarify previous ambiguities in the assignment of vibrational bands, especially accidental coincidence of CO and N_2O bands. The fragmentation dynamics exhibit the same unexpected behaviour as reported previously in which, once CO loss channels are energetically accessible, these dominate the fragmentation branching ratios, despite the much lower binding energy of N_2O . We have investigated the dynamics computationally by considering anharmonic couplings between a relevant subset of normal modes involving both ligand stretch and intermolecular modes. Discrepancies between correlated and uncorrelated model fit to the *ab initio* potential energy curves are quantified using a Boltzmann sampled root mean squared deviation providing insight into efficiency of vibrational energy transfer between high frequency ligand stretches and the softer intermolecular modes which break during fragmentation.

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1. Introduction

Isolated (*i.e.*, gas-phase) mixed ligand ion–molecule complexes provide a unique and well-defined environment in which to study important physico-chemical phenomena. These can include molecular activation at the charge centre (commonly a metal ion or cluster), cooperative and competitive binding effects, as well as energy flow within the complex. Infrared photodissociation (action) (IRPD) spectroscopy represents a powerful technique for such studies yielding information on non-covalent interactions, solvation and structural isomers.^{1–5}

Generating mixed-ligand complexes represents an additional level of challenge over simple ion–molecule species and, consequently, with the exception of inert tagging,^{3–11} relatively few spectroscopic studies have been undertaken on multiple ligand systems: Lisy completed systematic IRPD

studies on a range of small hydrated alkali metal complexes ($\text{M}^+\text{L}(\text{H}_2\text{O})_n$; $\text{M} = \text{Na}, \text{K}$ and $\text{L} = \text{benzene},^{12–14}$ phenol,¹⁵ indole,^{16,17} acetonitrile,¹⁸ *n*-methylacetamide,¹⁹ C_6F_6 ²⁰ and tryptamine²¹). Beyer and coworkers have similarly studied a range of hydrated transition metal– CO_2 clusters by employing IRPD within an ion cyclotron resonance mass spectrometer.^{22,23} Recently, time-resolved 2D-IR spectroscopy has been applied to watch energy flow and frustrated intramolecular vibrational redistribution (IVR) in $\text{Re}(\text{CO})_n(\text{CH}_3\text{CN})_m^+$ complexes.²⁴

We have previously reported detailed IRPD studies of mixed CO and N_2O complexes of Au^+ and Rh^+ , characterizing structures and comparing fragmentation patterns following excitation of the near degenerate $\text{C}\equiv\text{O}$ and $\text{N}_2\text{O N}=\text{N}$ stretching modes, respectively.^{25,26} Qualitatively different behaviour is observed in each with the Au^+ complexes exhibiting purely nonclassical carbonyl bonding whilst cooperative effects in Rh^+ result in a mix of classical and non classical binding.^{27,28} The most significant differences, however were observed in the fragmentation dynamics with $\text{Au}(\text{CO})_n(\text{N}_2\text{O})_m^+$ exhibiting unexpected non-statistical fragmentation with preferential CO loss contrary to expectations based on relative ligand binding energies.

Both $\text{Au}(\text{CO})_x^+$ and $\text{Au}(\text{N}_2\text{O})_y^+$ complexes have been studied in detail by IRPD spectroscopy.^{28,29} In mixed-ligand complexes, the stronger binding of the CO leads to $\text{Au}(\text{CO})_x^+$ core structures

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with resulting blue-shifted $\text{C}\equiv\text{O}$ stretches ($2230 \pm 10 \text{ cm}^{-1}$). N_2O binds more weakly to this core with the $\text{N}=\text{N}$ stretch observed close to that in free N_2O (2223 cm^{-1}).²⁵ Our inability to resolve the CO and $\text{N}=\text{N}$ stretches presented an ambiguity in our previous spectral assignment which we address here. In this work, we report the IRPD spectroscopy of isotopically-selected $\text{Au}^{(12/13}\text{CO})_n(\text{N}_2\text{O})_m^+$ complexes. The fragmentation of these species provides insight into the dynamics of these processes and restricted energy flow within these complexes.

II. Experimental and computational methods

The spectrometer used in this work has been described in detail previously.^{26,30,31} All gas mixes used were 1% CO : 5% N_2O in Ar. In order to generate complexes with different $^{13}\text{CO}/^{12}\text{CO}$ ligand fractions the CO used ranged from 100% ^{12}CO to 100% ^{13}CO . The mass spectrum of species generated in a $^{12}\text{CO}:\text{N}_2\text{O}:\text{Ar}$ mix has been published previously²⁵ and so Fig. 1 shows a representative time-of-flight mass spectrum of $\text{Au}^{(13}\text{CO})_n(\text{N}_2\text{O})_m^+$ produced by laser ablation of an Au target in presence of 1% ^{13}CO , 5% N_2O gas mix in Ar and introduced at a backing pressure of 6 bar (see Fig. S1 in the ESI† for more a detailed spectrum). The distribution of species produced is qualitatively similar to that in our earlier work on the ^{12}CO mixed-ligand system.²⁵

The strongest ion signal observed is the $\text{Au}^{(13}\text{CO})_2^+$ species whose stability is an example of the Orgel effect.^{32,33} Other abundant species observed include $\text{Au}^{(13}\text{CO})_n(\text{N}_2\text{O})_m^+$ ($n = 0-5$, $m = 0-3$). Mass-selected infrared action spectra were recorded by selecting parent ions using a quadrupole mass filter. In some cases involving mixed $^{12}\text{CO}/^{13}\text{CO}$ ligands, complete separation proved impossible without unacceptable transmission losses.

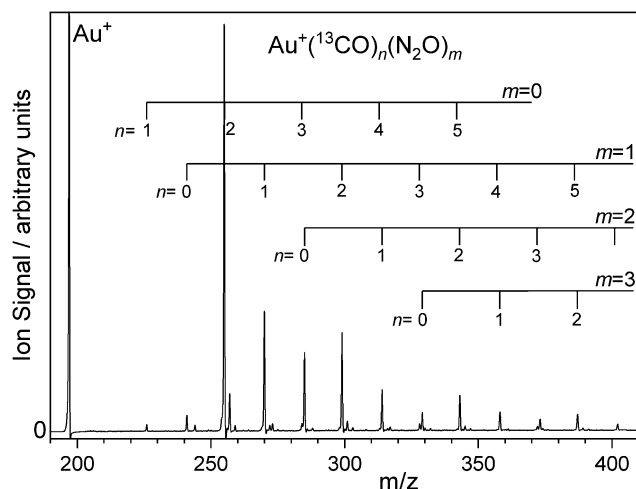


Fig. 1 Time-of-flight mass spectrum of $\text{Au}^{(13}\text{CO})_n(\text{N}_2\text{O})_m^+$ complexes produced by laser ablation of a gold target in presence of a carrier gas comprising 1% ^{13}CO and 5% N_2O in Ar. Complexes incorporating both ^{12}CO and ^{13}CO were produced with various mixes of the two isotopologues. *N.b.*, the vertical scale is chosen to highlight the complexes observed. The Au^+ signal at $m/z = 197$ is cropped.

However, the mass resolving power of the detection reflection time of flight mass spectrometer was sufficient to determine the fragmentation channels unambiguously. The ESI† includes the mass spectrum of $\text{Au}^{(13/12}\text{CO})_n(\text{N}_2\text{O})^+$ species along with photo-fragment mass spectra collected at $\tilde{\nu}_{\text{IR}} = 2157 \text{ cm}^{-1}$, 2207 cm^{-1} , and 2230 cm^{-1} illustrating that photofragmentation occurs by loss of CO , of N_2O or of both (Fig. S2–S4, ESI†). Gating the signal in different mass channels allows fragment-specific spectra to be recorded yielding information on the energy flow within the complex. The resulting fragmentation dynamics have been the focus of previous studies and we return to them here with isotopologue selectivity. First, however, it is necessary to understand the spectroscopy of the isotopically-labelled complexes.

To aid structural assignment, the IRPD spectra recorded are compared with those simulated for the lowest-energy isomeric structures determined at the B3P86-Def2TZVP level of theory^{28,34,35} which proved effective in our previous studies. All electronic structure calculations presented here were completed using Gaussian 16 program.³⁶ Scalar relativistic effects were included with the use of the ECP60 effective core potential for the Au^+ ion. All low-lying structures identified were singlet states. Calculated line spectra have been convoluted with Lorentzian line-shapes to help comparison with the experimental data. Calculated harmonic frequencies rarely match observed bands well and it is conventional to scale calculated vibrational frequencies³⁷ for comparison with experiment. This is usually done by scaling the calculated frequency of a fundamental band to its known experimental value. This is challenging in systems with multiple (different) ligands. To a good approximation, as expected in relatively weakly-bound complexes, the bands observed in the spectral region covered by this study are well described as local N_2O or CO -centred modes. Hence, we have taken the approach of scaling such bands independently. For the B3P86-Def2TZVP level of theory, these factors are 0.9322 and 0.9626 for the N_2O $\text{N}=\text{N}$ stretch and the CO stretch respectively. Scaling using these factors results in simulated spectra as shown in Fig. S3–S5 in the ESI† which allow unambiguous identification of the observed spectral bands. However, while the N_2O -based bands match very well, the CO -based bands are slightly overscaled resulting in excessively red-shifted calculated spectra. To provide a better match with experiment, the Figures shown below have been scaled with factors generated by fitting two Lorentzian functions to the single peak in the $\text{Au}(\text{CO})_2(\text{N}_2\text{O})^+$ spectrum (Fig. 2). As the $\text{N}=\text{N}$ stretch is well reproduced by traditional scaling this peak position is fixed and the relative intensities of the two peaks is drawn from calculations. This yields a CO stretch peak position of 2230.7 cm^{-1} ($r^2 = 0.97933$) with resultant scaling factors of 0.9322 (N_2O) and 0.9674 (CO).

III. Results and discussion

(a) Infrared spectra of isotopically selected $\text{Au}^{(12/13}\text{CO})_2(\text{N}_2\text{O})^+$ complexes

Fig. 2 shows a comparison of the infrared spectra for the isomer-selected $\text{Au}^{(12/13}\text{CO})_2(\text{N}_2\text{O})^+$ complexes with those



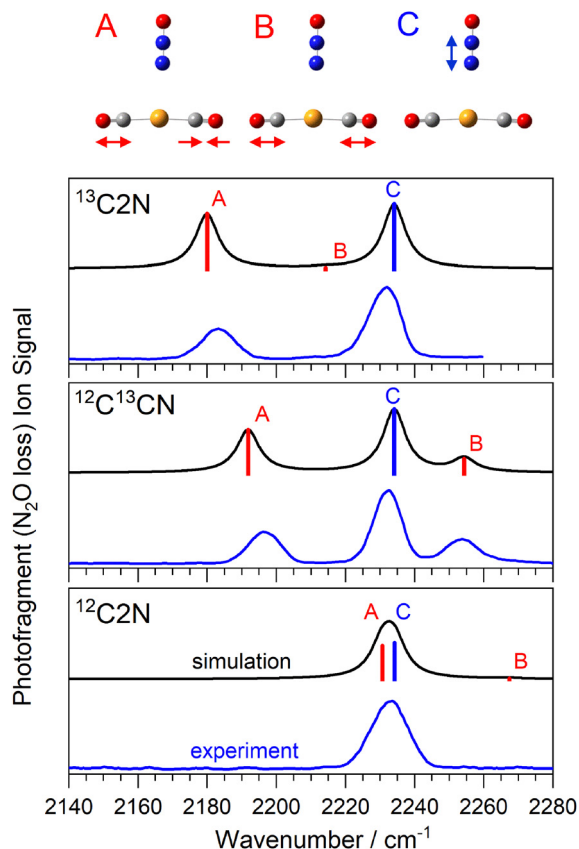


Fig. 2 Comparison of experimental and simulated infrared action spectra of $\text{Au}^{(13/12)\text{CO}}_2(\text{N}_2\text{O})^+$ complexes. Vibrational modes observed comprise the anti-phase CO stretch (A), in-phase CO stretch (B, with meaningful oscillator strength only in the mixed $^{12}\text{C}^{13}\text{CO}$ isotopologue) and the N_2O ($\text{N}=\text{N}$) stretch (C) as shown above.

simulated for the lowest energy calculated structures. This spectral region covers (i) the anti-phase and in-phase CO stretching bands in the $\text{Au}(\text{CO})_2^+$ core (labelled A, and B, respectively) and (ii) the N_2O $\text{N}=\text{N}$ stretch fundamental (labelled C). For brevity, we introduce a new nomenclature in which structures are labelled based on the number of ^{13}CO or ^{12}CO equivalents, so the $\text{Au}^{(13}\text{CO})(^{12}\text{CO})(\text{N}_2\text{O})^+$ isotopologue is labelled $^{13}\text{C}^{12}\text{CN}$, and the $\text{Au}^{(13}\text{CO})_2(\text{N}_2\text{O})^+$ complex $^{13}\text{C}_2\text{N}$. The spectrum of the $^{12}\text{C}_2\text{N}$ complex is reproduced from our original article.²⁵ In all three isotopologues, only the simple N_2O loss channel is observed, reflecting the highly stable $\text{Au}(\text{CO})_2^+$ core to which the N_2O binds more weakly. Hence all the spectra shown are recorded as enhancements, from a zero baseline, in the $\text{Au}(\text{CO})_2^+$ mass channel.

The spectrum of $^{12}\text{C}_2\text{N}$ complex in this region (Fig. 2) comprises a single, broadened (*ca.* 14 cm^{-1} full width half-maximum, FWHM) peak at approximately 2233 cm^{-1} . As discussed previously,²⁵ we are unable to resolve the N_2O $\text{N}=\text{N}$ stretch fundamental from the anti-phase CO stretch in this peak. Confirming this accidental degeneracy was one of the inspirations for this study as the isotope shift of ^{13}C should eliminate it. The N_2O $\text{N}=\text{N}$ stretch (labelled C) lies very weakly blue-shifted from the free N_2O band (at 2223.5 cm^{-1}) reflecting

its weaker binding to the core structure. This is also indicated by the $\text{Au}-\text{N}$ distance, determined by DFT calculations to be 3.026 Å. By contrast, the CO vibrational bands are strongly blue-shifted from the free CO stretch at 2143 cm^{-1} reflecting their “non-classical carbonyl” nature^{27,28} arising from the cationic metal center and the resulting lack of π -back-bonding. The very near linear $\text{Au}(\text{CO})_2^+$ core means that the in-phase CO stretch band has very weak oscillator strength (labelled B, near 2270 cm^{-1}) and is not observed.

Isotopic substitution of a single ^{12}CO with a ^{13}CO leads to two major changes in the spectrum. Firstly, both CO-stretching bands are notably red-shifted from their band positions in the $^{12}\text{C}_2\text{N}$ spectrum reflecting the smaller reduced mass and its effect on the vibrational constant ($\omega_e \propto \sqrt{\frac{k}{\mu}}$). Secondly, the reduced symmetry results in intensity in both the in-phase and anti-phase CO stretching bands which are observed at $\sim 2253 \text{ cm}^{-1}$ and $\sim 2195 \text{ cm}^{-1}$, respectively.

The spectrum of the $^{13}\text{C}_2\text{N}$ complex, as expected, shows two clear bands, the $\text{N}=\text{N}$ stretch (unchanged in all isotopologues) and the anti-phase CO band at 2183 cm^{-1} , *ca.* 45 cm^{-1} to the red of the equivalent band in $^{12}\text{C}_2\text{N}$. The in-phase stretching band is again essentially symmetry forbidden.

In all cases, the simulated spectra reproduce the experimental spectra remarkably well, leaving little doubt over the security of the assignments. This provides confidence in assigning the larger complexes. In a more general context, this ability to reliably move vibrational modes within mixed ligand complexes *via* isotope substitution offers hope in better resolving, and hence understanding, the spectra of other ion-molecule complexes.^{28,29,38,39}

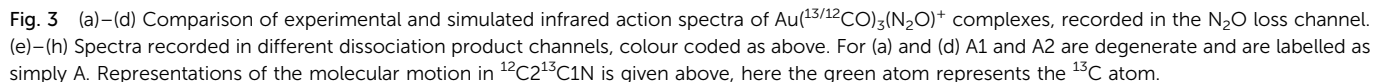
(b) Spectra and fragmentation branching ratios of larger mixed-ligand complexes

Fig. 3 shows the comparison of experimental and simulated spectra for the four isotopologues of the $\text{Au}^{(12/13)\text{CO}}_3(\text{N}_2\text{O})^+$ complex. The structure is unambiguously assigned to a C_{3v} structure with trigonal planar $\text{Au}(\text{CO})_3^+$ core to which N_2O binds along the C_3 axis *via* the terminal N atom.²⁵ The addition of a third CO to the core brings the calculated CO binding energy down from 0.7 eV to 0.26 eV, still markedly higher than the 0.15 eV binding of the N_2O ligand but accessible for IR photodissociation in the range of our spectra (0.265–0.282 eV).

The spectra in Fig. 3a–d were recorded in the N_2O loss channel for direct comparison with Fig. 2. Only two bands are IR active in the spectrum of the $^{12}\text{C}_3\text{N}$ and $^{13}\text{C}_3\text{N}$ complexes, the $\text{N}=\text{N}$ stretch and the degenerate CO antisymmetric stretch (at 2206 cm^{-1} and 2155 cm^{-1} , respectively). New IR active modes arise in the $^{12}\text{C}_2^{13}\text{CN}$ and $^{12}\text{C}^{13}\text{C}_2\text{N}$ complexes as the CO symmetric stretch gains oscillator strength and the anti-symmetric stretch splits into two components (labelled A1 and A2).

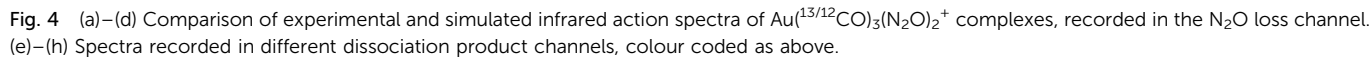
The markedly lower CO binding energy in C_3N complexes compared to C_2N complexes gives rise to more interesting fragmentation dynamics. Now multiple dissociation channels





Our experiments cannot distinguish unambiguously between two photon absorption followed by fragmentation and

The similarity of C3N2 complexes to C3N follows though into the fragmentation dynamics. Again the strongest branching ratios are observed for the CO loss channels although the effect is less marked in C3N2 given the second N₂O ligand.



To a good approximation, the relative single ligand fragmentation yields mirror the respective number of ligands present with the ratio of total CO loss to N₂O approximately 3 : 2. This despite the calculated CO binding energy (at 0.26 eV) being a factor of two larger than that for N₂O (0.12 eV).

Once more, near identical spectra are observed in all the single ligand loss channels further supporting the idea of rapid IVR. The additional N₂O ligand further exaggerates the relative prominence of the N₂O band in the dual ligand loss channels. In the ¹³C¹²CN₂ complex barely any CO bands are observed in the –[CO, N₂O] channels whilst in the ¹³C¹²C₂N₂ complex only the A₂ CO mode exhibits meaningful oscillator strength in these channels. Interestingly, in both the ¹²C₃N₂ and the ¹³C₃N₂ the CO bands are extremely weak in the dual –[CO, N₂O] loss channels. No fragmentation was observed corresponding to either –2CO or –2N₂O fragmentation despite the latter having comparable dissociation threshold to single CO loss.

The vibrational motion associated with each of the calculated modes is very local to the chromophore excited. That is to say that excitation of the N₂O stretches result in almost no motion of the CO ligands and *vice versa*. This is particularly true in the symmetric C₃N₂ complexes with Au(N₂O)₂⁺ and Au(CO)₃⁺ systems vibrating completely independently. Even in the C₂N and C₃N complexes, the motion induced in the CO-system following excitation of the N₂O vibration is minimal.

(c) Computational study of intramolecular energy flow

In an attempt to better understand the dissociation dynamics observed a nudged-elastic band optimization^{41,42} was performed to estimate the minimum energy path for N₂O and CO dissociation. The Gaussian 2016 program was again used for all electronic structure calculations.³⁶ The result is shown in Fig. 5 with full details provided in ESI.† The abscissa coordinate

is the distance between the gold atom and the centre of mass of the leaving ligand. Three cuts across the potential energy surface (PES) are shown, relative to the minimum energy structure, with figures of the path enclosed in the same colour as the cut. The lowest (black) potential corresponds to loss of the N₂O ligand, while the red and blue cuts correspond to different pathways leading to CO loss; The CO-*p* (red) curve corresponds to CO leaving within the plane of the CO core and the CO-*o* (blue) curve a path orthogonal to the trigonal plane. The two are similar except in the close-range region in which CO-*o* is steeper. CO cleavage can clearly occur *via* heat transferred to vibrational motion perpendicular to, or in, the trigonal plane. The threshold for N₂O loss (0.17 eV), is, however, markedly lower than that for CO loss (0.30 eV) and the preferential loss of CO observed experimentally remains hard to explain on energetic grounds.

IR absorption by a localized vibrational mode heats the rest of the complex *via* anharmonic terms in the potential energy surface. Although the system undergoes substantial geometric changes upon dissociation, the early transfer of energy out of the initially excited zero-order bright state is driven by small anharmonic coupling terms. To analyse the coupling between modes and how these can lead to competing dissociating pathways, whilst keeping the analysis tractable, we have partitioned modes into subsets corresponding to stretches and intermolecular ligand modes. Since the number of CO ligand modes is large, we selected those which are necessarily involved in the formation of the co-linear CO, C₂N complex (approximately half of them). These also naturally describe the in-plane dissociation seen in Fig. 5. To estimate the correlated space between modes, we proceeded to evaluate the PES. For every pair of modes possible, vectors along the diagonal of each quadrant were used to evaluate tens of *ab initio* samples. We also generated hundreds of quasi-random (Sobol) samples for these same correlated spaces (see Fig. S8 in ESI†). Mass- and frequency-scaled normal mode coordinates were used to approximately place all displacements into a similar domain. A cluster expansion of symmetry-adapted polynomial functions was then fitted to the calculated data.⁴³ Up to sixth order polynomials were used to fit the data with minimal error (typical average RMSD below 10^{–5} eV).

To estimate the mode-pair correlation more accurately, the following root mean squared deviation (RMSD) $\sigma_{\text{corr}} = \sqrt{\langle \Delta V_{\text{corr}} \rangle^2}$, was numerically estimated using a Monte-Carlo approach such that:

$$\langle \Delta V_{\text{corr}}^2 \rangle = Z^{-1} \int \exp\left(\frac{-V(\vec{x})}{k_B T}\right) ((V(\vec{x}) - V_{\text{uncorr}}(\vec{x}))^2 d\vec{x}, \quad (1)$$

where k_B is the Boltzmann constant, T the temperature and Z the canonical normalization function. $V(\vec{x})$ is the model PES in the pair of coordinates space while $V_{\text{uncorr}}(\vec{x})$ corresponds to the model PES without any correlating (cross) terms. The integral measures the degree of correlation in the regions of phase-space accessed by the system at temperature T . This is done for each possible pair of modes and averaged for each set using a sampling temperature of 150 K which represents a reasonable

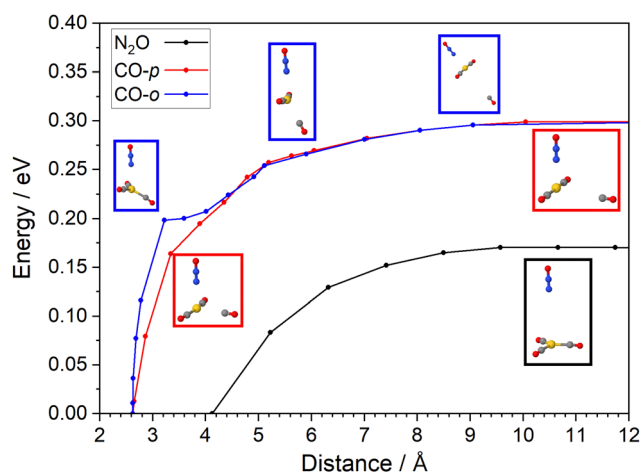


Fig. 5 Minimum energy paths for the dissociation of CO and N₂O ligands. CO-*p* (red) corresponds to a path that retains the trigonal plane as CO dissociates. CO-*o* (blue) corresponds to CO dissociation in an orthogonal to the trigonal plane. The x-axis shows the distance between the centre of mass of the ligand to the gold atom.



Table 1 Correlation matrix between different sets of modes. The correlation corresponds to the averaged RMSD difference between the correlated and uncorrelated cluster-expansion models fitted to the *ab initio* data. Values are scaled to the N₂O ligand–N₂O ligand term (3.25×10^{-2} eV) for ease of comparison

	CO stretch	N ₂ O stretch	CO ligand	N ₂ O ligand
CO stretch	0.02	0.0004	0.05	0.24
N ₂ O stretch		0.02	0.001	0.02
CO ligand			0.05	0.03
N ₂ O ligand				1.00

estimate of the experimental conditions. Table 1 shows the average (relative) RMSD values of the various mode-pairs scaled to the N₂O ligand–N₂O ligand term (3.25×10^{-2} eV) to illustrate their relative magnitude. This provides a more quantitative measure of the extent of coupling between the differing types of motion.

Table 1 shows that the stretching modes couple comparably well with their respective ligand modes. However, CO stretching also couples strongly to N₂O ligand modes and conversely, N₂O stretching modes weakly couples with CO ligand modes. This appears contrary to the experimental observation that pumping either CO or N₂O stretches leads to effective and similar CO fragmentation. However, time-dependent perturbation theory suggests population transfer depends not only on coupling, but inversely on frequency difference. In this case, N₂O ligands may consequently take longer to become excited; N₂O ligand dissociating modes (modes 1a, 2a, see Table S3: around 50–70 cm^{−1}, ESI†) have lower frequencies than the corresponding CO ligand modes (modes 4–6e, 1a₂ and 3a₁, 4a₁ ranging from 200 to 450 cm^{−1}).

The CO ligand modes couple significantly to all modes (except the N₂O stretch). Those CO ligand modes not included in the subset (orthogonal to the trigonal plane) are also likely to couple to the in-plane modes since these must be, at least in part, involved in the out-of-plane dissociation (blue) profile of Fig. 5. Together, this trigonal framework forms a large anharmonically-coupled manifold plausibly ‘funneling’ the available energy, such that stretch excitations may well preferentially heat the intermolecular CO ligand vibrations faster than the intermolecular N₂O ligand vibrations.

Table 1 alone is not sufficient to explain the non-statistical experimental results and a closer examination is warranted. The ongoing construction of a model PES on which to perform quantum dynamical simulations, which will form the basis of a subsequent article, is briefly described here. We use ‘quasi-normal’ coordinates which succinctly represent the competing dissociating channels, while continuing to form a basis for C_{3v} irreducible representations; this allowed us to accurately fit the Taylor model to the anharmonic basins, whilst permitting a further fit of the dissociating channels. This product-form model allows the application of wave packet methods⁴⁴ for which we can measure the picosecond energy transfer from high to low frequency modes, as well as the outgoing flux along the dissociating channels.

IV. Summary and conclusions

¹³CO substitution has been used to better understand the structure and spectroscopy of mixed ligand Au⁺(CO)_n(N₂O)_m ion–molecule complexes. The agreement between experimental infrared action spectra and simulated vibrational spectra of calculated low energy structures is good and provides for unambiguous identification of the structures generated. Similar action spectra are observed in all single-ligand loss channels indicating rapid intramolecular vibrational redistribution following infrared absorption. Only N₂O loss is observed for Au⁺(CO)₂(N₂O) complexes, reflecting the strong binding of the Au⁺(CO)₂ core structure. No clear isotopologue effects were observed in the dissociation yields with ¹²CO vs. ¹³CO loss in stoichiometric ratios within experimental uncertainty. In Au⁺(CO)₃(N₂O)_{1,2} complexes, however, a clear preference for CO loss is once more observed over N₂O loss despite the binding energy for the latter being considerably smaller. This non-statistical fragmentation has been investigated computationally both by computing vibrational mode couplings on an *ab initio* potential surface and with nudged elastic band dissociative potential energy curves. The former yield insight into potential bottlenecks in the energy flow around the complex following vibrational excitation, with coupling between the CO–Au⁺ intermolecular modes and the N₂O stretch particularly weak. Weak coupling between the CO ligand modes and the N₂O ligand modes together with the larger phase space of the former, suggest that energy may be effectively trapped in the Au⁺(CO)_n core leading to more efficient CO loss than N₂O when energetically allowed.

Conflicts of interest

The authors declare no competing financial interests.

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