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Infrared spectra of strongly bound clusters: Extending the limits of action spectroscopy

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6 Spectroscopic evidence for dissociative adsorption of carbon monoxide on niobium clusters

Abstract

The adsorption of CO on gas-phase niobium clusters is investigated with infrared multiple photon depletion spectroscopy. Gas-phase anionic, neutral or cationic niobium clusters are produced in a laser ablation source. Downstream in a reaction channel the formed clusters interact with CO molecules leading to the formation of Nb_nCO . Infrared (IR) depletion spectra for Nb_nCO clusters ($n = 3 - 8$) in the $150 - 2200 \text{ cm}^{-1}$ spectral range are recorded using the Free-Electron Laser for Intra-Cavity Experiments (FELICE).

The spectra exhibit resonances below 800 cm^{-1} , but not in the $1200 - 2200 \text{ cm}^{-1}$ spectral range where the CO stretching vibration is expected, thereby providing spectroscopic evidence of dissociative binding of CO. Density functional theory (DFT) calculations are carried out and the comparison between calculated and experimental IR spectra leads to assignment of several observed spectra to unique structures where the C and O atoms are integrated in the cluster.

6 Spectroscopic evidence for dissociative adsorption of carbon monoxide on niobium clusters

6.1 Introduction

The interaction between carbon monoxide and metal surfaces is one of the best characterized processes in surface science due to its relevance for catalytic processes.¹⁴⁹ An example is the Fischer-Tropsch process where hydrocarbons are produced from a mixture of CO and H₂ (syngas). With depleting natural resources of fossil fuels and the accompanying rise in fuel prices, this process is receiving an increased attention, due to its potential to make liquid fuels from *e.g.* biomass^{150;151}. These reactions are heterogeneously catalyzed by a range of transition metals (TMs)¹⁵².

The binding of CO to metal surfaces is often discussed in conjunction with a model introduced by Blyholder¹⁰¹, a variation of the well-known Dewar-Chatt-Duncanson model^{99;100}. This model is described in Section 2.3. Shortly, CO donates electron density in a bonding σ -orbital with some π -backdonation from the metal to the CO, weakening the internal CO bond. If this backdonation is sufficiently strong, the carbon monoxide bond will break altogether and CO binds dissociatively. A fundamental question here is thus whether the molecule stays intact after binding or whether it dissociates on the surface. For bulk metal surfaces the answer to this question is known: for the late TMs molecular adsorption dominates while for the early transition metals dissociative adsorption prevails^{153–155}. This effect is driven rather by the decrease in M-O and M-C binding energy when going to later TMs than by a difference in the M-CO binding energy, which is relatively constant for all TM elements.

The discovery of the enhanced catalytic activity of supported gold clusters in CO oxidation¹² led to a renewed interest in the adsorption of CO on gas-phase TM clusters containing a few to several hundred atoms. Their isolation in the gas phase and the formation of cluster-CO complexes allows for a controlled study of their interaction, as the use of mass-spectrometric techniques enables the study of size- and charge-dependent variations rather than ensemble averaged properties. Due to their finite size and isolation from external influences these systems are amenable for high-level quantum chemical calculations assisting in the elucidation of the interaction. These microscopic studies also provide benchmark data for the modeling of catalytic processes on a macroscopic scale.

Research on the reactivity of carbon monoxide with TM clusters dates back to the 1980s^{6;156;157}, when it was found that CO readily chemisorbs onto clusters of most (but not all) TM from a certain minimum cluster size¹⁵⁶. These studies, in which the collision between cluster and CO took place in the presence of helium background gas, showed a rather smooth increase in the reactivity as a function of niobium cluster size although a slightly lower reactivity was found for Nb₁₀¹⁵⁶. Holmgren *et al.*¹¹ addressed the sticking probability of CO on neutral niobium clusters in the single-collision regime and found more pronounced fluctuations as a function of cluster size with a distinct minimum in reactivity for Nb₁₀. Above $n = 20$, the sticking probability of CO on Nb_{*n*} is found to be near-unity.

Balteanu *et al.*¹⁵⁸ have compared the chemisorption rate constants for anionic

and cationic clusters from group 5 and 9 metals and for smaller cluster sizes ($n < 20$) found a distinct reduction in rate constant for group 5 anionic clusters with respect to their cationic counterparts. This has been rationalized as the result of an elastic repelling of the CO upon approaching the group 5 cluster anion by the electron cloud. The effect was not observed for group 9 cluster anions where the extra electron is more confined due to the higher electron affinity of these metals.

The nature of CO binding to transition metal clusters could not be unambiguously established by these studies. It is generally believed that the binding type is determined by the metal type, but surface structure and reaction conditions may also play a role. To answer this question structure-sensitive information is required. Fielicke *et al.*¹⁵⁹ have investigated the modes of binding by measuring the infrared (IR) spectra of TM clusters with CO adsorbed. To this end, they formed TM-CO complexes by adsorbing gaseous CO onto TM clusters formed through laser ablation. By measuring the depletion of TM-CO they obtained IR spectra for CO adsorbed on clusters of several late TM elements¹⁶⁰⁻¹⁶⁶. In all these systems, a depletion at a frequency characteristic for a CO stretching vibration was found, leading to the conclusion that CO binds molecularly to these species.

For complexes between CO and early TM clusters, however, no depletions in the 1400 - 2200 cm^{-1} region could be found, pointing to a dissociatively bound CO^{167;168}. For Nb_3CO an extensive study combining several techniques has been performed¹⁶⁷, also suggesting dissociative binding on the basis of IR spectroscopy and DFT calculations. Later, Addicoat *et al.*¹⁶⁹ performed a DFT study on the binding of CO to $4d$ TM clusters with three metal atoms, which showed that at the global minimum for Nb_3 carbon monoxide is dissociatively bound. Clearly, so far the results are based on theory and the absence of a depletion, which is rather unsatisfactory. It can after all not be ruled out that the IR excitation efficiency in the experiments mentioned above is not high enough to induce dissociation in the experimental time window.

Recently, we have developed experiments where beams of TM clusters can be subjected to IR radiation within the cavity of the Free-Electron Laser for Intra-Cavity Experiments FELICE¹³⁶. In these experiments, clusters and cluster-adsorbate systems can interact with IR photon fluxes that are up to two orders of magnitude higher than in the original apparatus used for TM cluster-CO studies. Using this instrument, we have demonstrated the IR induced photodetachment of niobium and niobium carbide anion clusters down to frequencies of 100 cm^{-1} .⁷¹

We here set out on experiments characterizing the structure of Nb_nCO cluster complexes with two aims: first, if CO binds molecularly, a higher IR photon flux may enable the observation of depletion due to a CO-stretch vibration which may have escaped detection earlier. Second, it may enable studying the low-frequency part of the spectrum where the niobium-carbide and niobium-oxide vibrations are located. This part of the spectrum has received much less attention than the CO-stretching frequency region, since the vibrations involving the metal have much lower absorption cross sections and are thus more difficult to observe. Measuring

this part of the spectrum may lead to detection of multiple absorption bands facilitating the elucidation of Nb_nCO clusters structure in detail by comparing the experimental spectra with calculated spectra for several different structures as obtained by density functional theory (DFT) calculations.

6.2 Materials and methods

The IR-MPE experiments are performed using the instrument on the first beam line of FELICE, described in detail in Chapter 3. Niobium clusters (cationic, neutral and anionic) are produced in a Smalley-type laser ablation source. The second harmonic (532 nm) of a pulsed Nd:YAG laser is focused onto a rotating solid niobium rod (Aldrich Chem. Co., 99.8% pure). A short helium gas pulse, injected with a pulsed valve (General Valve Series 9) cools the formed plasma and promotes cluster formation through carrier gas mediated collisions in a clustering channel (3 mm diameter, 60 mm long). The channel is extended by a 44.5 mm long copper channel which is liquid nitrogen cooled to ~ 80 K. Here a small amount of CO is introduced in the gas pulse which adsorbs onto the niobium clusters. The end of the channel is formed by a converging diverging nozzle (~ 0.6 mm diameter) through which the gas pulse is expanded into vacuum. The molecular beam is skimmed first by a 2 mm skimmer and, after traveling through a differential vacuum, by a slit (4x0.45 mm). Both apertures can be electrically biased to prevent ions formed in the ablation process from entering the interaction region, used when measuring the spectrum of the neutral species. In the interaction region the cluster beam is crossed by the FELICE IR laser beam under an angle of 35° .

After interaction with FELICE, the charged species are pulse-extracted into a the reflectron time-of-flight (RETOF) mass spectrometer (Jordan TOF Products, Inc.), with a typical mass resolution of $M/\Delta M \approx 1700$. The neutral species are, after interaction with FELICE, first ionized with an ArF excimer laser (193 nm) and afterwards pulse-extracted into the RETOF mass spectrometer, with a typical mass resolution of $M/\Delta M \approx 1700$. Transients from the MCP detector are recorded with a 400 MSample/s 100 MHz digitizer (Acqiris DP310). To account for fluctuations in the cluster source, a reference mass spectrum is recorded between every two FELICE pulses. The experimental IR spectra are obtained by plotting the ratio between the intensities of the mass channels in the FELICE mass spectrum and the reference mass spectrum. In theory, a mass channel could be completely depleted, however a maximum depletion of $\sim 70\%$ was observed. A possible cause is that the cross-section of the cluster beam is larger than that of the FELICE beam. All spectra for a specific charge state are recorded simultaneously in a multiplexing fashion.

6.3 DFT calculations

To allow for the assignment of experimental IR depletion spectra density functional theory (DFT) calculations are carried out for several trial structures. Due to the large parameter space and the computational cost of DFT calculations at a level that is sufficiently accurate, the most difficult task is the generation of trial structures and the selection of the most promising candidate structures. Here, random trial structures are generated with as limitation a minimum and maximum distance between each constituent atom, ensuring a reasonable minimum bond length and a starting structure that is at the least close to a bound system. Although these limitations may provide a bias towards compact structures, the comparison between the resulting calculated IR spectra and the experimental spectra suggest an efficient probing of parameter space. All trial structures are submitted to a full geometry optimization using the Becke exchange with Perdew's 1986 correlation functional^{87,90} (B-P86) and a split valence (def2-SVP) basis set.⁹⁴ No symmetry is imposed.

All trial structures where the geometry optimization succeeded have been analyzed by their energy and geometry to verify whether they represent distinct or identical geometries. Typically, the ten lowest-energy geometries from this analysis have been selected and submitted to a further geometry optimization using the same B-P86 functional, now with a triple zeta (def2-TZVP) basis set⁹⁴ and with more stringent convergence criteria. For these structures harmonic frequencies and IR intensities are calculated. For each cluster size, the lowest energy structures and their calculated spectra are presented in Figures 6.3 - 6.7. The harmonic frequencies are convoluted with a Gaussian lineshape (FWHM 10 cm^{-1}), and the y-axes are scaled with the same factor for all geometries found for a certain cluster size. All DFT calculations are performed using the TURBOMOLE V6.3 suite of programs.⁸⁵

For each cluster size, runs of fixed calculation time have been carried out. Since the computational cost of DFT calculations scales non-linearly with the number of atoms this means that the total number of succeeded initial geometry optimization yields large numbers for the smaller cluster sizes, whereas for the larger species only few structures have been found.

When performing a search for structures of metal clusters, many different geometries are conceivable. For the larger clusters where only a few structures have been found, the possibility of "missing" the true minimum structure is very real. An example is the structure determination of Nb_{13} as discussed in Section 5.3.3, where the lowest energy structure was not found at first. The larger number of different structures found for the smaller clusters, together with the high number of successful geometry optimizations, so that most structures were found multiple times, gives more confidence of a proper sampling of the conformational space. However, a match between a calculated spectrum and the experimental spectrum is of itself a strong indication that the true structure has been found, regardless of the numbers.

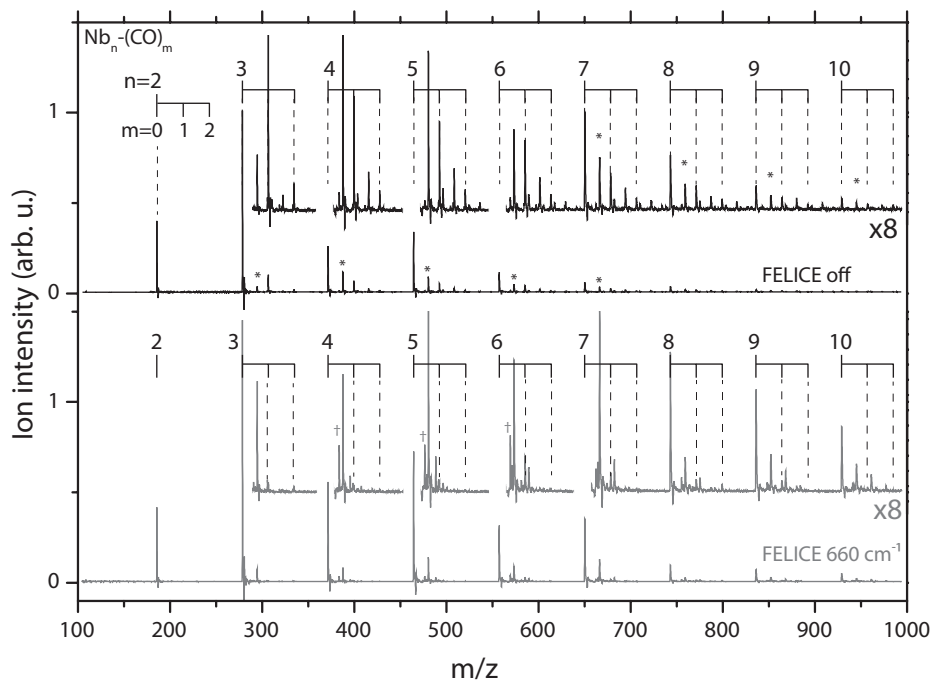


Figure 6.1: Mass spectra for neutral $\text{Nb}_n\text{-(CO)}_m$ clusters without FELICE irradiation (top trace, black) and with FELICE tuned to 660 cm^{-1} (bottom trace, gray). The amount of Nb atoms and CO adducts is indicated. Impurities in the mass spectrum are indicated by asterisks (Nb_nO) and crosses (Nb_nC).

All calculations were done assuming the lowest-spin electronic ground state. For the lowest energy structures higher-spin states have been examined as well. For neutral and cationic Nb_nCO structures all higher-spin states are found higher in energy than the lowest spin state. For anionic systems and the cationic $\text{Nb}_3\text{-CO}$ clusters, calculations yielded mixed results; as a consequence, the lowest energy structures are presented. If necessary, also the higher spin state IR spectra are shown and the structures are ordered by the energy of the lowest energy states.

6.4 Results and Discussion

A TOF mass spectrum for neutral Nb_nCO clusters (ionized with 193 nm after interaction with FELICE) is shown in Figure 6.1. The top trace exhibits a reference mass spectrum which is taken without FELICE. This mass spectrum gives an indication of the composition of the cluster sample prior to irradiation with

FELICE. The most intense signals are formed by pure niobium ($m_{\text{Nb}} = 92.9$ amu) clusters for which the sizes are indicated. The niobium cluster distribution shows a maximum for Nb_3 , but cluster sizes up to Nb_{10} are observed, as shown in the zoom where the vertical scale is enlarged by a factor of 8.

On the high mass side of each niobium cluster, several satellite peaks are visible. The first, at a distance of 16 amu, represents Nb_nO (indicated with asterisks). Oxide impurities are often present in metal cluster distributions from early TMs. The $\text{Nb}_n\text{-CO}_m$ ($m = 1, 2$) peaks are indicated by the dashed lines. Their intensities are rather small and a critical dosing of the CO quantity is required to avoid growth of clusters with more than one CO adsorbed. If the intensity of mass peaks with more than one CO is appreciable with respect to that for a single CO, IR induced fragmentation of $\text{Nb}_n(\text{CO})_m$ into the Nb_nCO mass channel may obscure the depletion spectra recorded for Nb_nCO . No CO uptake by the Nb_2 cluster is observed and the relative amount of CO adducts increases for larger clusters. This effect has been observed previously^{6;158} and is attributed to the increasing cluster surface area. The intensities of the anionic, neutral and cationic Nb_nCO ($n = 3 - 8$) peaks are sufficiently high, so that spectra can be recorded.

The bottom trace in Figure 6.1 has been recorded after irradiating the cluster sample with FELICE tuned to 660 cm^{-1} . The Nb_nCO clusters are clearly substantially depleted. At the same time, one observes an *increase* in the Nb_n and Nb_nO channels. In the inset (again an eight-fold expansion of the ordinate) it is also visible that there is an increase in some of the Nb_nC mass channels. It is difficult to relate the various mass channel intensities to the IR absorption of Nb_nCO . It is *e.g.* known that Nb_nC_m clusters absorb strongly in this frequency range which leads to thermionic emission¹³⁵. Similarly, it is expected that Nb_nO clusters also absorb in this region. For these reasons, the safest way to record a spectrum for Nb_nCO clusters is to record the depletion as a function of IR frequency, provided that the intensity ratio $\text{Nb}_n\text{CO}:\text{Nb}_n(\text{CO})_2$ prior to irradiation is high.

6.4.1 Overview experimental IR spectra

The experimental IR depletion spectra are obtained by taking the ratio of the detected ion current for the specific Nb_nCO mass channel in the mass spectrum recorded with and without irradiation by FELICE, respectively. The spectra are shown in Figure 6.2 where they are organized by size and charge state. The spectra are distinctly different for each cluster size and charge state, although certain trends are visible. Almost all spectra have one or more peaks in the $500\text{-}800\text{ cm}^{-1}$ spectral range which can be attributed to metal-oxide and metal-carbide vibrations. For each charge state there is an apparent trend where the resonances shift gradually towards the red for larger systems. This is attributed to the higher reduced mass in the normal modes for larger clusters.

In determining the nature of the binding of carbon monoxide onto TMs, an important indication is the presence of a band in the $1400\text{ - }2200\text{ cm}^{-1}$ spectral range characteristic for the CO-stretch vibration¹⁵⁹. DFT calculations for Nb_nCO

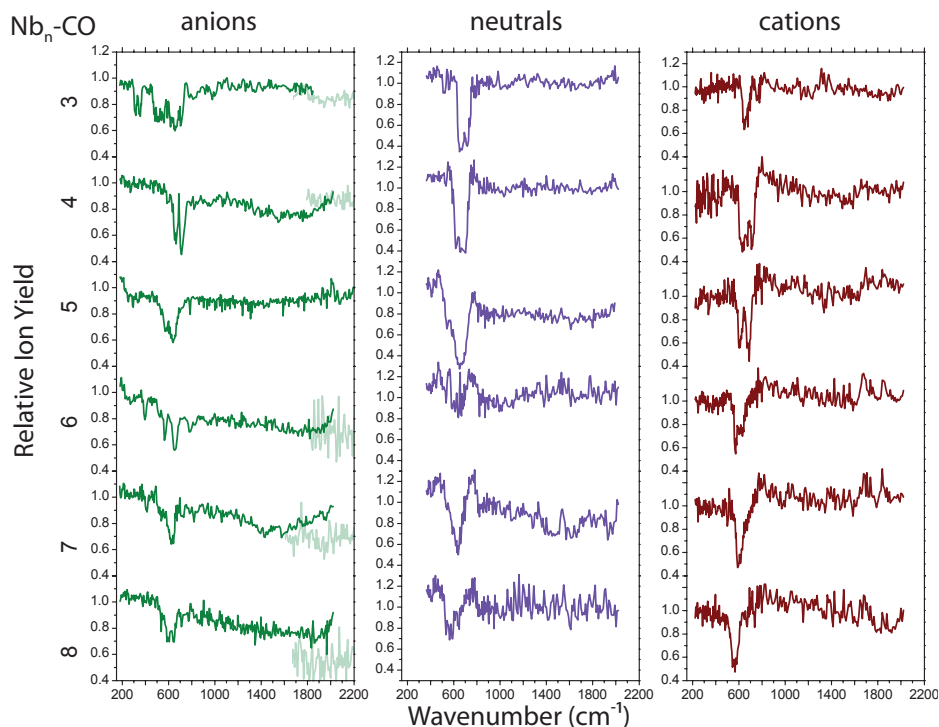


Figure 6.2: Overview of the experimental spectra. The columns are the different charge states and the rows are the different cluster sizes. The anionic trace in the 2000 - 2200 cm^{-1} spectral range is of low quality and thus not averaged with the other data.

clusters yield structures with an intact CO bond, however these are all at least 80 kJ/mol higher in energy than the lowest energy structure and thus not shown in the discussion of the individual spectra. Furthermore, these calculations indicate CO stretch vibrations between 1400 and 1900 cm^{-1} , or even lower if both carbon and oxygen are bound to the niobium cluster. The absorption cross section is large compared to the other vibrations in the spectrum; calculations predict that it can easily be a factor of ten larger. If an intact CO bond were present, a depletion in this frequency range would thus be expected to dominate the experimental spectrum. While the spectra exhibit depletions in this spectral range, they are very weak, broad and unstructured. If these broad depletions are compared to the sharp structures in the 500 - 800 cm^{-1} spectral range, it is unlikely that they are the result of strong and localized CO stretching vibrations. Broad and structureless absorption characteristics have been observed previously in the present experimental setup for pentacene and coronene cations and are attributed

to a “continuum” of combination modes.¹⁷⁰ From this, it is concluded that a CO stretching vibration is not present and that the previous conclusions regarding a missing CO vibration cannot be attributed to an inefficient IR excitation, thereby confirming the conclusions of dissociative bonding drawn by Pedersen *et al.*¹⁶⁷

6.4.2 Individual spectra

From the discussion above and from Figure 6.2 it is seen that the IR depletions characteristic for each cluster size are found in the spectral region below 800 cm^{-1} . In this region, vibrations involving NbC and NbO bonds are expected and as such they should form a sensitive probe for the structure of the dissociative complex. To be able to assign the recorded spectra to specific cluster structures, they are compared to spectra obtained *via* DFT calculations for various candidate structures. Below, the spectra for the individual cluster sizes are discussed. As no resonant structure is observed above 1000 cm^{-1} , the spectra are only shown in the $200 - 1000\text{ cm}^{-1}$ spectral range in Figures 6.3 - 6.7.

Below each experimental spectrum, calculated IR spectra are displayed for the lowest-energy structural isomers. The harmonic frequencies, calculated at the B-P86/def2-TZVP level, are not scaled. To facilitate comparison with the experimental data the stick spectra are convoluted with a Gaussian lineshape function with an associated FWHM of 10 cm^{-1} .

Nb₃-CO

Figure 6.3 shows the experimental IR depletion spectra of anionic (left), neutral (middle) and cationic (right) Nb₃CO. Although one would expect a rather simple IR spectrum for a 5-atomic species, the spectrum of anionic Nb₃CO exhibits quite a complex structure: two distinct depletions at 313 and 352 cm^{-1} are identified, there is a broad feature centered around 530 cm^{-1} and there is a broad structured depletion with distinct maxima at 590 , 658 and 712 cm^{-1} . None of the resonances exhibits a depletion that exceeds 30 %, but the shape of the depletion centered around 658 cm^{-1} suggests that this may be saturated.

All calculated spectra shown are for structures with the CO dissociatively bound. Structures with a molecularly bound CO are higher in energy by more than 80 kJ/mol . This is consistent with the lack of a depletion in the high-frequency spectral range characteristic for CO stretching vibrations. Although niobium clusters are generally assumed to be in the lowest possible spin state, for three structures the triplet state was found to be lower in energy than the singlet state, and hence spectra for both spin states are provided. From the spectra shown, none provides a clear match with the experimental spectrum, but if the typical number of resonances in the calculated spectra is compared to the number of observed resonances it appears likely that multiple isomers are present. The singlet 3A1 matches the depletions in the low energy part of the spectrum (at 313 and 352 cm^{-1}) and also has depletions in the higher energy region. However, in

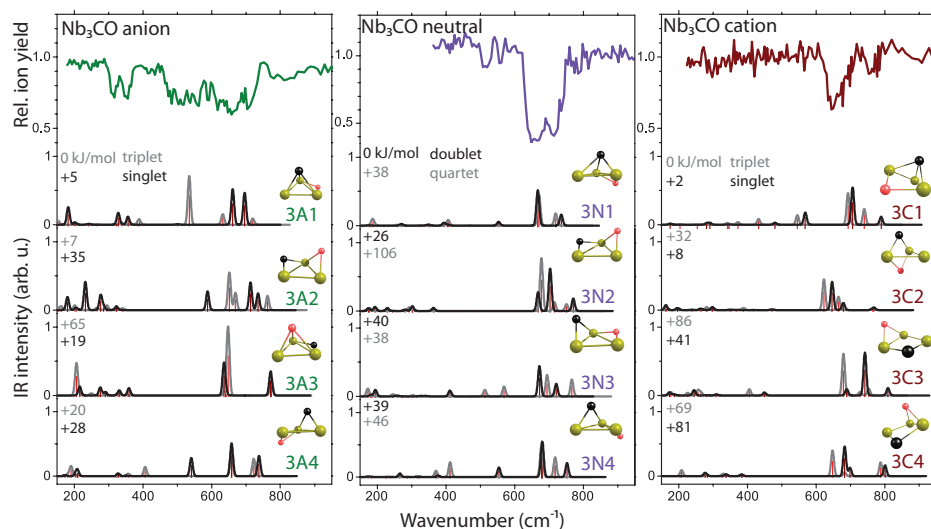


Figure 6.3: IR depletion spectra for anionic, neutral and cationic Nb_3CO . Below each experimental spectrum calculated spectra for several low-energy structural isomers.

the middle part of the spectrum, between 450 and 600 cm^{-1} structure 3A1 exhibits no vibrations. The triplet state, 5 kJ/mol lower in energy, does have a resonance in the middle part, although only one, while the experimental spectrum has a broad feature, possibly indicating more than one resonance. The singlet state of structure 3A4 also has a resonance in this spectral range and is 28 kJ/mol above the global minimum.

The spectrum of the neutral Nb_3CO is simpler than that for the anion. Only three clear depletions are visible at 517 , 660 and 717 cm^{-1} . The depletion at 660 cm^{-1} is the most intense and appears to be saturated while the depletion at 517 cm^{-1} is relatively small.

Although Pedersen *et al.*¹⁶⁷ found that the quartet states were much higher in energy than the doublet states, we found competitive energies for some structures. Therefore, the IR spectra of both the doublet and quartet spin states are shown. Pedersen *et al.*¹⁶⁷ found a structure reminiscent of 3N2 as the lowest energy geometry. Interestingly, the current investigations yield a structure (3N1) lower in energy by 40 kJ/mol or 0.4 eV at this level of theory.

The low number of depletions make it plausible that only one structure is responsible for the observed spectrum. The spectra of the 3N1 structures match the experimental spectrum reasonably well, although also 3N3 and 3N4 show the double peak at the high energy end.

The spectrum of the cationic Nb_3CO cluster shows two distinct depletions,

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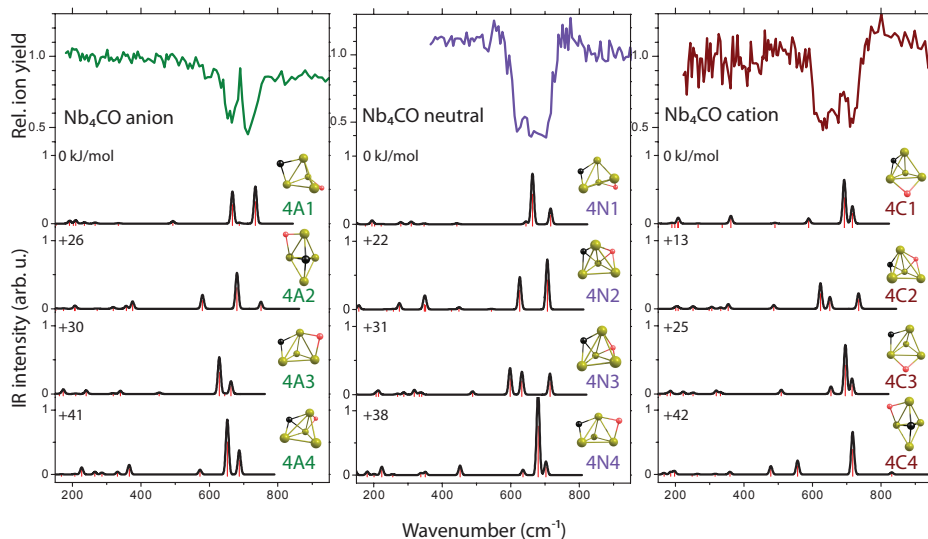


Figure 6.4: IR depletion spectra for anionic, neutral and cationic Nb_4CO . Below each experimental spectrum calculated spectra for several low-energy structural isomers.

one at 650 cm^{-1} and one at 760 cm^{-1} . Four calculated structures are shown. The lowest energy structure, 3C1, has a third peak at lower energy where no resonance is observed in the experimental spectrum and is excluded on these grounds. Of the other three structures, the singlet 3C2, triplet 3C3 and 3C4 states have a rather similar spectrum, which resemble the experimental spectrum, making it likely that the cationic Nb_3CO species has one of these structures.

$\text{Nb}_4\text{-CO}$

In Figure 6.4 the experimental IR depletion spectra for anionic, neutral and cationic Nb_4CO are shown. Below the experimental spectra several low-energy structures are shown together with their calculated spectrum and relative energy.

The experimental spectrum for anionic Nb_4CO clusters exhibits two major depletions at 660 and 713 cm^{-1} and a minor feature at 595 cm^{-1} . All structures found in the geometry search are doublet species and exhibit a tetrahedral core of Nb where the C and the O form two bonds each to the tetrahedron. The exception is formed by structure 4A2, 26 kJ/mol higher in energy than the lowest-energy structure found (4A1), where the C is integrated in the cluster structure forming a bicapped pyramid. Although in some cases (4A2 and 4A3) the quartet state was found to be competitive in energy with the doublet state, their IR spectra were nearly the same and thus only the spectra for the doublet states are shown.

The spectra are quite sensitive to the differences in the exact position of C and O. The spectrum of the lowest energy structure, 4A1, matches the two major depletions in the experimental spectrum rather well, with a Nb-C stretching vibration at 734 cm^{-1} and a Nb-O stretching vibration at 667 cm^{-1} . However, it does not explain the feature at 595 cm^{-1} , so there might be a small amount of another isomer present, for example 4A2 or 4A3.

In the experimental spectrum of the neutral Nb_4CO cluster there are two major depletions, at 618 and 680 cm^{-1} . To the red, at 529 cm^{-1} , is a third, smaller, peak. The four lowest energetic structures are shown (energy within 40 kJ/mol of the lowest energy structure). Structure 4N2 appears to match the experimental spectrum best, with calculated vibrations at 626 and 707 cm^{-1} and also a vibration at 544 cm^{-1} with only a small absorption cross-section. Structure 4N1 is excluded based on the intensity ratio of the two resonances.

The experimental spectrum for cationic Nb_4CO shows three overlapping depletions, at 631 , 672 and 718 cm^{-1} . The four lowest energetic structures (within 45 kJ/mol of the lowest energy structure) are shown together with their calculated spectra. None of these show a very good match, although 4C1 and 4C3 have the most intense peaks where the main feature in the experimental spectrum is located.

Nb₅-CO

In Figure 6.5 the experimental and calculated spectra are shown for Nb_5CO , where each charge state (anion, neutral, cation) is in a separate column.

The experimental spectrum of the anionic Nb_5CO shows two depletions, one at 580 cm^{-1} and one at 640 cm^{-1} . The DFT calculations yielded singlet spin states as minima for three of the four structures shown, but the triplet spin state was found to be lower for 5A3. Therefore, calculated IR spectra are shown for both spin states. Several of the calculated spectra have two strong absorptions, located at the same position as in the experimental spectrum. The experimental spectrum shows at the low-energy end something that might be noise or small depletions, so the isomer assigned to this species also needs to have no or very weak absorptions here. This suggests a combination of structures 5A1 and 5A2, however 5A4 cannot be excluded.

The experimental spectrum of the neutral species shows three depletions, at 413 , 544 and 660 cm^{-1} . The calculated structures with an energy less than 35 kJ/mol above the lowest energy structure are shown. The best match with the experimental spectrum is the spectrum belonging to 5N1, the lowest energy structure.

Three depletions are contained in the cationic Nb_5CO experimental spectrum, at 342 , 606 and 684 cm^{-1} . At the high energy end of the spectrum, the best match is with the calculated spectrum of 5C1, however, the experimental 342 cm^{-1} peak does not match with the calculated spectrum. This might come from 5C2, where peaks at the blue end are mixed with the 5C1 peaks.

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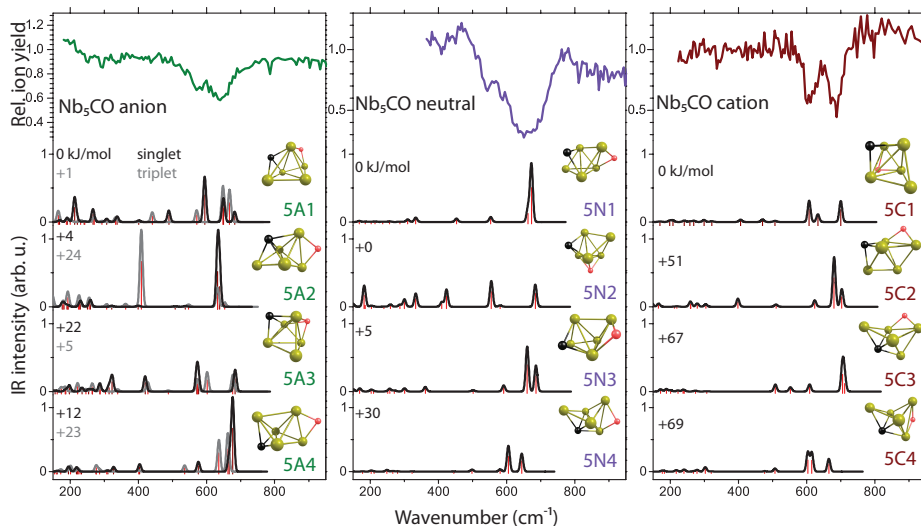


Figure 6.5: The experimental spectra for the three different charge states of Nb₅CO with below them the calculated spectra for the structures shown.

Nb₆-CO

The experimental spectra for the Nb₆CO species are shown in Figure 6.6. On the left is the spectrum for the anionic cluster, showing several depletions. The lowest energy depletion is at 397 cm⁻¹, followed by three bands at 520, 566 and 655 cm⁻¹ and there is a smaller depletion at 790 cm⁻¹. Below the experimental spectrum are the calculated spectra of structures within 100 kJ/mol from the lowest energy structure. Since the experimental spectrum and the calculated spectra are highly structured, the lowest energy structure can be assigned with confidence. The only mismatch is the peak at 790 cm⁻¹, which cannot be explained by any of the calculated spectra. It is possibly the result of a combination band.

In the center are the experimental and calculated spectra for the neutral cluster, indicating calculated structures within 110 kJ/mol of the lowest energy structure. Because of the poor quality of the experimental spectrum, no assignment can be made.

On the right is the experimental spectrum of the cationic species, showing two depletions at 572 and 627 cm⁻¹, which partly overlap. Below are the four calculated structures which were within 110 kJ/mol of the lowest energy structure. None of them matches the experimental spectrum particularly well, since all of them have either too many or too few depletions. For these bigger sized clusters fewer different isomers have been found than for the smaller cluster sizes. This is partly because the calculations are more expensive, so in the same amount of time

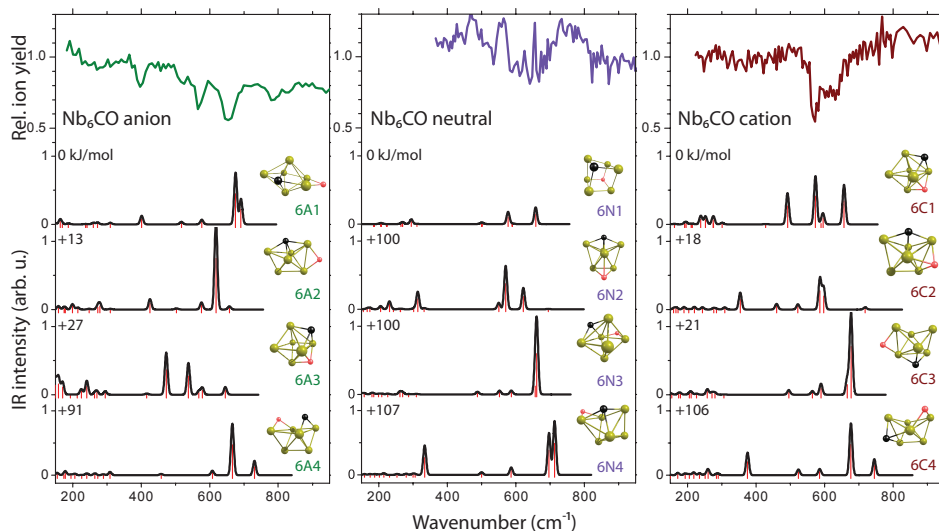


Figure 6.6: Experimental spectra for the three charge states of Nb_6CO and below the calculated spectra of the four lowest energy structures.

fewer structures have been optimized, but also because these calculations tend to have more problems converging. Thus, it might be that the correct structure has not been found.

$\text{Nb}_7\text{-CO}$

The experimental spectra for the Nb_7CO clusters are shown in detail in Figure 6.7. Below them are calculated spectra of the possible structures shown. Though in principle the more atoms a system has, the more possible structures, we could only find these isomers. For the cationic and anionic species even only one minimum was found.

The spectrum of the anionic Nb_7CO cluster shows four depletions, at 410, 543, 628 and 723 cm^{-1} . Even though we have only one calculated structure, it appears to be a good match, because the spectrum has the four strongest depletions also at these positions. The calculated spectrum also has several weak features at the low-energy end of the spectrum, but these might be so weak they disappear in the noise of the experimental spectrum.

The spectrum of the neutral species also has four depletions, at 409, 499, 539 and 635 cm^{-1} . The lowest energy structure, similar to the anionic cluster structure, seems to be the best match here too.

In the spectrum of the cationic Nb_7CO cluster only one peak is visible around 590 cm^{-1} . The match with the calculated spectrum of the only structure found is

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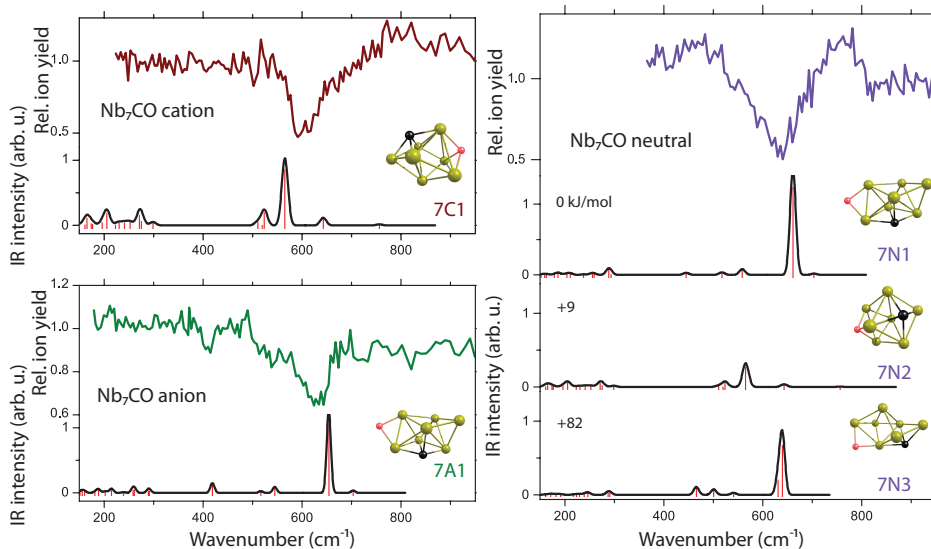


Figure 6.7: The experimental spectra for the three different charge states of Nb_7CO compared with calculated spectra.

not very good, so the cluster probably does not have this structure.

6.4.3 Discussion

The spectra described and discussed in the previous sections can all be ascribed to structures where CO dissociates upon binding to the niobium cluster. It is now of interest to relate the structures of the Nb_nCO clusters to those of the bare Nb_n clusters. We focus on discussing the clusters for which clear assignments have been made and those where no clear assignment to a specific candidate structure has been possible, but the candidate structures have shown at least highly similar motifs. Upon comparing the structures of bare Nb_n clusters with those of their Nb_nCO counterparts, it appears that no major structural re-arrangements in the Nb_n framework is induced by adsorption. In all cases, the C and O atoms are adsorbed to the exterior of the cluster. In most cases the oxygen binds in a bridging (μ^2) position, except for neutral Nb_4CO and cationic Nb_5CO , where the oxygen binds in a hollow (μ^3) position. The carbon atom, which has four valence electrons that typically form four bonds, does so when the cluster becomes large enough, from Nb_6 . When the niobium cluster is smaller, the cluster body prevents the formation of four bonds and the C typically is found in a μ^3 position. Interestingly, the structures assigned for anionic Nb_4CO and neutral Nb_5CO exhibit the C in a bridging configuration.

For anionic Nb_6CO , we do observe a structural re-arrangement. Here, the

C inserts itself in the Nb_6 cluster structure, forming a pentagonal bipyramid, with the O bridging on the pyramid base. For cationic Nb_6CO the lowest energy structure retains the cationic Nb_6 cluster structure, but the experimental spectrum is not decisive to assign a structure. For the few structures found in the search for neutral Nb_7CO , the two structures matching the recorded spectra best both have a niobium network resembling the distorted bipyramid shape of Nb_7 , albeit further distorted by the addition of the C and O atoms.

The vibrations observed in the current work are typically found in the 500 - 800 cm^{-1} spectral range. Below this region, resonances are difficult to discern, likely caused by the relatively low signal-to-noise (S/N) ratio that obscures detection of weaker resonances. The low S/N ratio in turn is partly caused by the low number of Nb_nCO species produced.

The most intense features observed are typically associated to vibrations involving Nb-C-Nb and Nb-O-Nb bond stretching and bending. The frequencies where the most intense bands are found coincide with the region where spectra are reported for neutral Nb_nC_m clusters, measured with IR-REMPI.¹³⁵

6.5 Conclusion

Size and charge state selective infrared spectra have been measured for niobium clusters with a carbon monoxide molecule adsorbed. For the anionic, neutral and cationic $\text{Nb}_{3-8}\text{-CO}$ clusters, no depletion has been observed in the CO-stretch region while in the region for the NbC and NbO vibrations depletion has been observed. Observation of these weaker modes, but not the intense CO-stretch indicates that the carbon monoxide dissociates upon adsorption on niobium clusters. This is further confirmed by DFT calculations, which show that molecularly adsorbed species are much higher in energy. For several clusters the experimental spectrum was sufficiently detailed to assign a tentative structure based on the match with one of the calculated spectra.

To assign structures to the other species based upon their IR spectra it would be necessary to extend the spectra further to the red. For ionic species this could be accomplished by a different formation of the $\text{Nb}_n\text{CO}^{+/-}$ cluster. Instead of producing them in a reaction channel, where Nb_nC and Nb_nO species are simultaneously formed, mass-selected clusters could be stored in a radio-frequency ion trap where small doses of CO could be introduced. In this more controlled environment, background-free spectroscopy could reveal more detailed spectra. The current study provides positive evidence for the dissociative binding of CO to niobium clusters. It holds the promise that in future studies of cluster-reactant systems, even the strongest bound systems can be structurally characterized.