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Far-Infrared spectroscopy of isolated transition metal clusters

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Abstract. The vibrational far-infrared (IR) spectra of isolated metal clusters in the gas phase can be measured by performing photo dissociation spectroscopy of their rare gas complexes. For these experiments an intense and widely tunable source of far-IR radiation is required, and the Free Electron Laser for Infrared eXperiments (FELIX) is ideally suited for this. Vibrational spectra are obtained for vanadium cluster cations as well as for neutral and cationic niobium clusters. The comparison of the experimental vibrational spectra with theoretically calculated spectra allows for the determination of the structure of the metal clusters.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 82.80.Gk Analytical methods involving vibrational spectroscopy

1 Introduction

The knowledge of the structural properties of a particle is vital for the understanding of its chemical and physical behavior. It is not at all straightforward to obtain accurate structural information of isolated clusters in the gas-phase, however. One experimental approach to obtain some information is to measure the cross section of the particle, as is done in ion mobility experiments [1,2]. A preferred approach is to measure the vibrational spectra of the clusters [3], as this probes the internal geometric structure and the binding situation in the cluster more directly.

To enable spectroscopic investigations on gas-phase clusters, the measurement method needs to be applicable to a very dilute sample, and it therefore needs to be many orders of magnitude more sensitive than direct absorption measurements. The latter can be achieved when the response of the cluster after photon absorption is monitored, rather than the absorption of the photons itself. This response of the system can, for instance, be a change of the charge state (ionization or electron detachment) or a change of its mass (dissociation). The measurement method also needs to be size specific, i.e., the method has to involve mass selection prior to the spectroscopic investigation and/or mass spectrometric detection afterwards. When both requirements are fulfilled, the measurement of the IR absorption spectra of clusters of a well-known composition becomes possible. It is clear, however, that ionization of a cluster in the IR spectral region involves the absorption of multiple photons. Similarly, most fragmentation processes require higher energies than those that are provided by a single IR photon. Therefore, an intense source of pulsed IR radiation is required for these experiments. To be able to measure the complete IR absorption spectrum of a cluster, the source has to be widely tunable throughout the (far-) infrared spectral region as well. Both characteristics can be met by free electron lasers and the experiments presented here are performed at the “Free Electron Laser for Infrared eXperiments” (FELIX) user facility at the FOM Institute “Rijnhuizen” [4] in the Netherlands.

During the last years, FELIX has been successfully used to investigate a variety of metal compound clusters. For strongly bound clusters with rather low ionization potentials, such as for example carbides of Ti, Zr, V, Nb, and Ta or oxides of Ti, Zr, Mg, and Al, infrared resonance enhanced multiple photon ionization (IR-REMPI) spectroscopy has been applied to record IR spectral properties of the neutral clusters [3,5]. IR spectra of other metal oxide clusters, such as for example the oxides of vanadium [6,7], niobium and tantalum [8], have been obtained via infrared multiple photon dissociation (IR-MPD) spectroscopy. In the case of small vanadium oxide clusters, where direct photodissociation turned out to be difficult to achieve, the dissociation of weakly bound rare gas complexes has been used to monitor the IR absorption [7]. For some of these group V transition metal oxide clusters, the comparison between the experimental spectra and the calculated spectra for various possible structures has proven to be a viable approach to determine the structure of

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the clusters. In addition to these studies, the IR-MPD technique has been used to investigate the internal vibrational modes of ligands in various metal cluster complexes, such as Ag_nNH_3, $Rh_nCO^{+/0/-}$, and $V_nH_2O^+$ [9]. In these studies, however, no direct information on the internal structure of the metal cluster core could be obtained so far.

Vibrational spectra of small metal clusters have been measured by performing matrix isolation spectroscopy on accumulated and embedded mass selected clusters [10,11] as well as on clusters aggregated directly in the matrix [12]. In some cases, vibrational structure has been identified in gas-phase clusters in electronic excitation spectra [13–18]. In our recent study on vanadium cluster cations V_n^+ in the size-range of $n = 6$–23, we have reported the first far-IR absorption spectra of isolated metal clusters in the gas-phase [19]; a more detailed discussion of these experiments and a comparison with theory for the clusters V_n^+ ($n = 3$–15) will be given elsewhere [20]. The far-IR spectra of the vanadium clusters have been obtained via photodissociation of complexes of the metal cluster cations with rare gas atoms, a technique that has previously been used to measure the optical absorption spectra of some transition metal clusters [21–25]. In these weakly bounded complexes, the metal cluster forms the chromophore and the rare gas atoms are expected to have a negligible influence on the cluster structure; the rare gas spectator atoms merely serve to monitor the IR absorption process. Here we report on details of these far-IR photodissociation experiments and we particularly discuss the influence of the rare gas ligands on the experimentally observed IR spectra.

2 Experimental

The experiments are performed in a molecular beam set-up that is coupled to the beam-line of FELIX and that has largely been described before [3,26]. Here, some experimental details are given that are relevant for the far-IR photodissociation studies of the cold metal cluster complexes. A scheme of the experimental set-up is shown in Figure 1. The clusters are produced by ablating a metal rod using the second harmonic output (532 nm, ~10 mJ) of a pulsed Nd-YAG laser. The subsequent injection of a short pulse (~100 μs) of a rare gas mixture, consisting mainly out of He, leads to cooling of the plasma and condensation within the 3 mm diameter and 12 mm long clustering channel. This channel is extended by a 30 mm long copper channel, with an inner diameter of 4 mm, on which a converging/diverging nozzle with an opening of 0.5 mm diameter is placed. The copper channel is thermally isolated from the main body of the cluster source by Teflon spacers and is cooled by direct contact to a liquid nitrogen filled reservoir. When the gas mixture contains a sufficient concentration of Ar and when the copper channel is maintained at about ~80 K, complexes of the metal clusters with Ar atoms can be observed. There appears to be substantial cooling during the expansion, since complex formation is found to strongly depend on the nozzle shape as well; with a flat nozzle plate, no Ar complexes are observed.

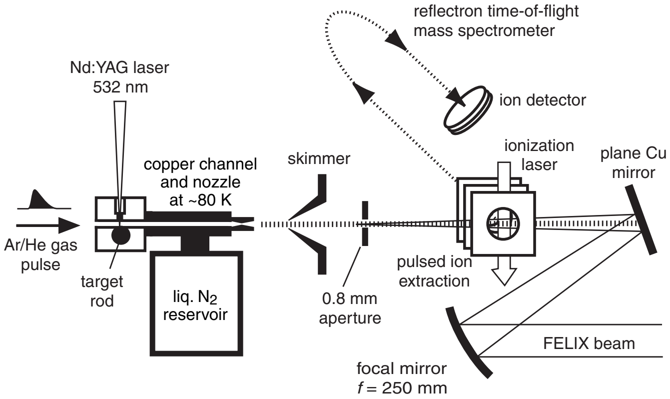

Fig. 1. Scheme of the experimental set-up used for IR multiple photon dissociation of metal cluster–rare gas complexes.

After expansion into vacuum, the molecular beam is shaped by a skimmer followed by an aperture of 0.8 mm diameter. The cluster distribution in the molecular beam is analyzed using a reflectron time-of-flight mass spectrometer (R.M. Jordan Company, Inc.). When studying neutral clusters, the charged clusters are deflected out of the molecular beam and the remaining neutrals are ionized using an ArF excimer laser (NEWEKS PSX-100; 6.4 eV/photon) or using the frequency doubled output of a dye laser.

The molecular beam is overlapped with the counter-propagating IR laser beam, delivered by FELIX. FELIX can emit tunable pulsed radiation throughout the 40–3500 cm^{-1} range but is here only scanned in the far-IR spectral region to excite vibrations of the metal clusters. The far-IR laser pulse consists of a train of 0.3–3 ps duration micropulses that are spaced by 1 ns in a 7 μs duration macropulse. The energy in the macropulse is typically 20 mJ. The IR beam is focussed onto the aperture in the molecular beam and is timed to irradiate the pulsed cluster beam when this is near the focus. When the frequency of the far-IR radiation is resonant with an IR active absorption of the cluster, one or more photons can be absorbed by the cluster. The excitation occurs typically 50 μs before the clusters arrive in the ion extraction region of the mass spectrometer. The resulting heating of the clusters may induce evaporation of the rare gas atoms, leading to depletion of the complexes in the beam. IR depletion spectra are constructed by recording the ion intensities of the rare gas complexes as function of the FELIX frequency. As the detection is mass selective, the simultaneous measurement of far-IR spectra for different cluster sizes is possible.

To correct for long term intensity fluctuations of the cluster source, the experiments are performed in a toggle mode with the cluster beam source running at 10 Hz and FELIX at 5 Hz. Using two different channels of a digital storage oscilloscope, mass spectra are recorded and averaged alternatingly, transferred to a computer and analyzed as described below.

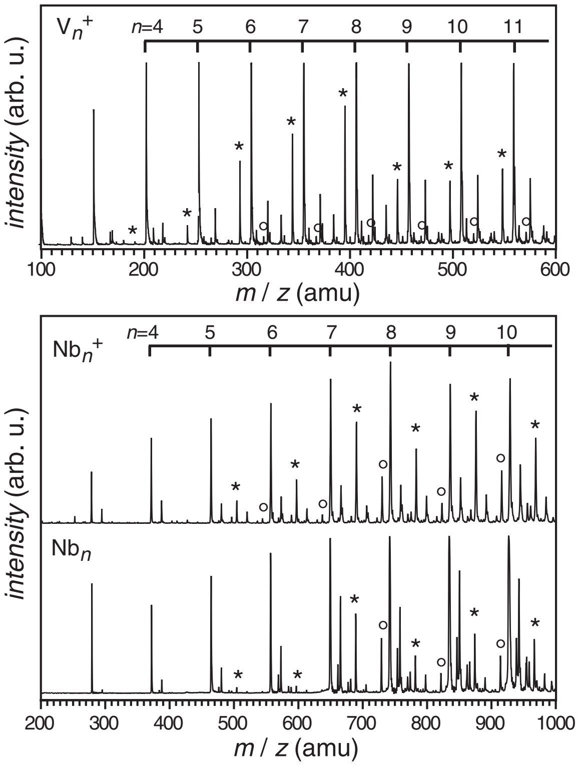

Fig. 2. Mass spectra of vanadium and niobium clusters and their complexes with Ar. The distributions are obtained using gas mixtures with Ar concentrations of 1% (V_n^+), 0.5% (Nb_n^+), and 40% (Nb_n) in He. The cationic cluster distributions are emitted directly from the source, whereas the neutrals are ionized using 6.4 eV photons. Complexes with one Ar atom are marked with an asterisk (∗), complexes with two Ar atoms with an open circle (○).

3 Results and discussion

3.1 Mass spectra

Mass spectral distributions showing the formation of Ar complexes for cationic vanadium as well as for cationic and neutral niobium clusters are presented in Figure 2. The amount of complex formation strongly depends on the concentration of Ar in the rare gas mixture. The spectra shown here are measured under conditions that have been optimized for the production of complexes containing only a few Ar atoms, but formation of some higher complexes often appeared to be unavoidable. For the cationic vanadium clusters, complex formation is observed already for the smallest sized clusters. For Nb clusters on the other hand, a strict onset of Ar complex formation is found at the five atom clusters. Interestingly, a clear maximum in the Ar complex intensities is found for the clusters containing seven V or Nb atoms. Since this effect is observed for the neutral as well as for the charged clusters, it does not seem to be related to a (charge induced) polarization effect (in the cations) or to the ionization energetics (for the neutrals) but rather to the geometry of the cluster. This enhanced affinity of $M_7^{+/0}$ towards rare gases is also observed for the heavier rare gas atoms, Kr and Xe. One could speculate that all seven atom clusters have similar geometries and that they exhibit favored sites for the binding of the rare gas atoms.

3.2 Far-IR absorption spectra

The far-IR absorption spectra are obtained by converting the measured depletion spectra to absorption cross-sections $\sigma(\nu)$ and by normalizing for variations of the laser intensity $P(\nu)$ over the tuning range using

$$\sigma(\nu) = \ln(I_0/I(\nu))/P(\nu)$$

where $I(\nu)$ and I_0 are the intensities of a certain $M_n\mathrm{Rg}^{+/0}$ complex with and without FELIX irradiation, respectively. This procedure assumes a one photon absorption process. Calculations for $\mathrm{Au}_4^+\mathrm{Ar}_x$ find binding energies of ∼0.1 eV per Ar atom [25] and also the adsorption energies of rare gases on metal surfaces are typically in the range of 0.1–0.2 eV [27]. It is expected from these binding energies that the photodissociation of cold rare gas complexes in the far-IR will be the result of a sequential multiple photon absorption process. Because of this, and also because the IR pulse energy as well as the spectral width and the shape and the size of the focussed beam are changing with wavelength (note that almost a factor three in wavelength is covered in this study), it is not at all clear if the applied normalization method suffices. However, in a recent study different approaches for extracting IR absorption spectra of cationic polycyclic aromatic hydrocarbons from observed IR-MPD spectra have been compared, and there it has been shown that the normalization approach used here can yield spectra that are very similar to one photon absorption spectra [28].

3.2.1 Influence of the rare gas

The far-IR multiple photon dissociation spectra of the mono- and di-Ar complexes of the vanadium heptamer cation are shown in Figure 3. More precisely, these are the far-IR depletion spectra as observed on the mass of the V_7Ar^+ and on the mass of the $V_7Ar_2^+$ complex, converted to frequency dependent cross-sections using the procedure described above. When observing the signal intensity on the $V_7Ar_2^+$ channel, two intense peaks are found, whereas on the V_7Ar^+ channel only one peak is present and the peak at lower wavenumbers is missing. This is observed for some other clusters as well: complexes having only one or two Ar atoms have bands missing that are observed for complexes having more rare gas atoms. These apparent missing peaks are experimental artifacts. In our experiment there is no mass selection of the complexes prior to fragmentation and only the product distribution is analyzed. Therefore, the depletion spectrum as recorded for a certain complex both contains the true depletion of that complex as well as the increase of the intensity

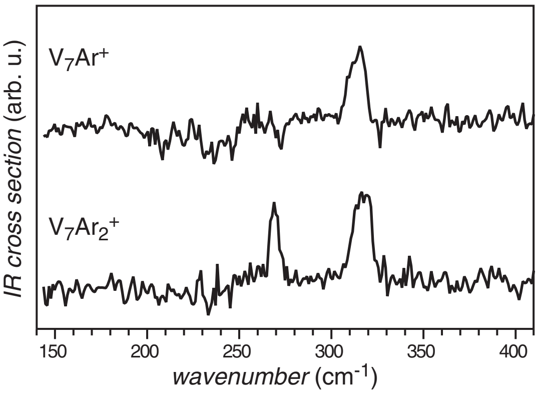

Fig. 3. Far-IR multiple photon dissociation spectra of V_7Ar^+ and $V_7Ar_2^+$.

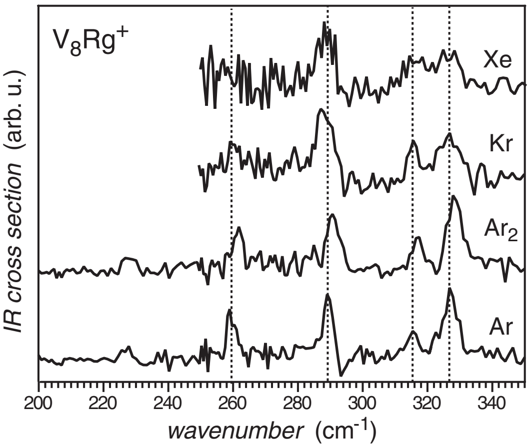

Fig. 4. IR spectra for V_8^+ complexed with different rare gases. The dashed vertical lines indicate the observed peak positions for V_8Ar^+.

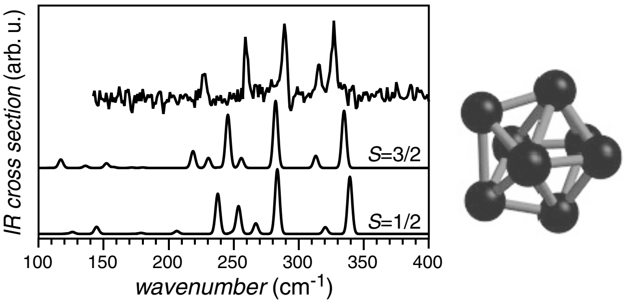

Fig. 5. Comparison of the experimental far-IR dissociation spectrum of V_8Ar^+ with the calculated IR absorption spectra for the lowest energy isomer of V_8^+ in the $S = 1/2$ and in the $S = 3/2$ spin state (adapted from Ref. [19]).

of that complex due to fragmentation of complexes containing more rare gas atoms, complicating the interpretation of the observed depletion spectra. These complications can be avoided when in the excitation of a complex with multiple rare gas atoms sufficient energy is provided to evaporate off all rare gas atoms. In particular at the low frequency end of the spectrum this is often difficult to achieve, however, and one thus has to be aware of such possible spectral distortions. In the case of V_7Ar^+ the band at 268 cm^{-1} is nearly completely missing, for example, while the band at 315 cm^{-1} seems only slightly affected.

The influence of the rare gas atoms onto the far-IR spectra can be studied further by substituting Ar with Kr or Xe. For this the V_8^+ cluster is chosen as this cluster has relatively narrow absorption bands, enabling a more accurate determination of band positions and of possible shifts of bands. In Figure 4 far-IR spectra are shown for four different V_8Rg^+ complexes. The spectra of the complexes with the heavier rare gases contain more noise due to their broader isotope pattern, leading to unavoidable overlap with the mass peaks of other species. The dashed vertical lines mark the peak positions for the V_8Ar^+ complex, and are indicated to more readily recognize possible peak-shifts in the other complexes.

In general, the spectra are very similar. The relative intensities of the IR bands are comparable for the complexes of V_8^+ with Ar, Kr and Xe. Only the low frequency band at about 260 cm^{-1} appears to have a lower relative intensity in the case of the Kr and Xe complexes. This could well be related to the stronger binding of the heavier, and more polarizable, rare gas atoms to the metal cluster, which makes the dissociation at lower photon energy less efficient. Part of the changes in the relative peak intensities might also be due to slight variations in the experimental geometry between the different runs and due to variations in the spectral and spatial profile of the FELIX radiation.

The peak positions are nearly identical for all V_8Rg^+ complexes. Only for the complex with two Ar atoms, a slight blue shift of the bands of about 1–2 cm^{-1} is observed. This shift is most likely due to the mechanism of the sequential multiple photon absorption followed by dissociation. The (cross-) anharmonicities that are important in a multiple photon excitation process generally lead to a spectral red-shift with increasing excitation. If we assume that the complex containing two Ar atoms is more readily dissociated than the complex containing one Ar atom, in line with a more general observation that we have made and that is discussed later, then a lower overall far-IR excitation of the complex is required for the $V_8Ar_2^+$ complex compared to the V_8Ar^+ complex, explaining the observed relative blue-shift. It should be noted that even though the width and positions of lines in the observed far-IR-MPD spectra can differ from those in the linear IR absorption spectra, any frequency shift is expected to be smaller than the bandwidth of the laser.

3.2.2 Structure determination

The experimental IR spectra form the basis for the determination of the geometric structure of the metal clusters. This is illustrated in Figure 5 by the comparison of the experimental IR-MPD spectrum of V_8Ar^+ with calculated IR absorption spectra for one structural isomer of V_8^+ in different spin states. The isomer with $S = 1/2$ is found to be the energetically lowest isomer, with the $S = 3/2$

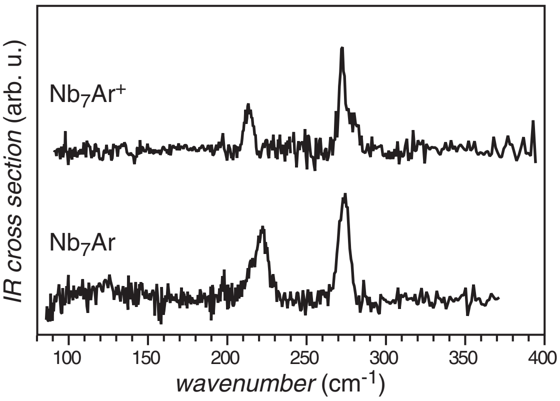

Fig. 6. Far-IR multiple photon dissociation spectra of the Ar complexes of the cationic and neutral niobium heptamers.

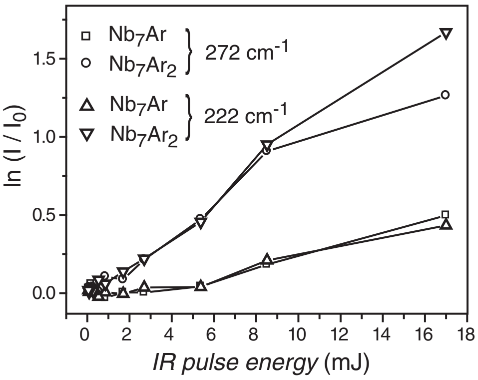

Fig. 7. Amount of depletion as a function of the pulse energy of the dissociation laser.

isomer 0.42 eV higher in energy. Good agreement is found between the experiment and either one of the calculated spectra. Calculated spectra of other investigated structures are found to be very different [19]. Together, this allows for the assignment of the structure of V_8^+ to the one shown on the right hand side in Figure 5. Details of the DFT calculations are given elsewhere [19,20].

3.2.3 Niobium clusters

The IR-MPD technique for obtaining IR spectra is generally applicable to metal clusters, as explicitly demonstrated here by the measurement of the far-IR spectra of clusters of niobium, the heavier homologue of vanadium. In Figure 6 the spectra of the Ar complexes of the cationic and neutral niobium heptamers are shown. As in the spectrum of $V_7Ar_2^+$ (see Fig. 3), two peaks are observed in both spectra, shifted to considerably lower wavenumbers in this case, however. The similarities between the IR dissociation spectra of $V_7Ar_2^+$, Nb_7Ar^+ and Nb_7Ar are striking and indicative of similar geometric structures for these metal clusters. This is in agreement with recent density functional theory studies that identify for all these heptamers a (distorted) pentagonal bipyramide as the most stable structure [29]. The average ratio of the absorption frequencies of $V_7Ar_2^+$ and Nb_7Ar^+ is 1.21, which can be compared to the value for $\sqrt{(m_{\mathrm{Nb}}/m_{\mathrm{V}})}$ of 1.35. Obviously, the experimental frequency ratio is too small to assign the observed shift solely to the mass effect; differences in the metal-metal bond strength between vanadium and niobium clusters clearly have to be included as well [10].

For Nb_7Ar and Nb_7Ar_2 the dependence of the dissociation yield on the pulse energy of the far-IR laser is studied, the results of which are shown in Figure 7 for the two absorption bands. A close to linear power dependence is found that is typical for all neutral and cationic metal cluster complexes. Importantly, this illustrates the validity of the normalization procedure described earlier. For Nb_7Ar_2 the slope of the curve in Figure 7 is found to be steeper by about a factor of three compared to the slope of the corresponding curve for Nb_7Ar. It is unlikely that this strong effect is due to a change in the absorption cross-section induced by the additional Ar atom. It is more plausible that Nb_7Ar_2 can more readily evaporate off one Ar atom. We have observed this for other species as well, i.e., we generally find that the complexes $M_nRg_x^+$ can be more readily dissociated upon IR excitation with an increasing number x of rare gas atoms. Although this could be due to the increasing number of (low frequency) vibrational modes that enhances the intramolecular vibrational energy redistribution, it seems more likely that the energy necessary to evaporate off a single rare gas atom decreases with increasing number of rare gas atoms. Besides (small) direct effects of the rare gas on the electronic structure of the cluster, the decrease of binding energy can be due to the inequality of different binding sites on the cluster. Similar findings have been reported for $Au_4^+Ar_x$ complexes in DFT calculations [25].

4 Conclusion

Multiple photon dissociation spectroscopy is used to measure the far-IR spectra of rare gas complexes of neutral as well as of charged metal clusters. In particular, studies on vanadium and niobium clusters have been undertaken. The rare gas atoms are found to have only a minor influence on the measured spectra. The obtained far infrared multiple photon dissociation spectra of the rare gas complexes of metal clusters thus resemble the far-IR absorption spectra of the corresponding bare metal clusters. The knowledge of these IR spectra allows for a determination of the cluster structure by comparison with theory. This new experimental information is expected to lead to a better understanding of the physical and chemical properties of metal clusters and to a better insight in the evolution of these properties with cluster size. The technique can be extended to chemically relevant cluster-adsorbate systems and enables a detailed study of the influence of the metal cluster structure on the chemical properties, as well as of the effect of the adsorbates on the cluster structure.

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