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# The effect of charge upon CO-adsorption by ionic group 5 and group 9 transition metal clusters

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## Abstract

Cold $M_n^{\pm}$ group 5 (V, Nb, Ta) and group 9 (Co, Rh, Ir) cationic as well as anionic clusters with up to about 30 atoms were produced by laser vaporization in supersonic expansion, and their reactivity with carbon monoxide was investigated in an FT-ICR mass spectrometer under conditions of bimolecular collisions. Anionic and cationic clusters of the later, group 9 transition metal elements, as well as cations of group 5 exhibit very similar behavior and trends. While the smallest species, $n \leq 4$ are almost unreactive under the conditions of our experiment, for larger clusters above $n = 5$ the rate of CO attachment increases abruptly by at least three orders of magnitude. On the other hand, a strikingly different behavior is found for the group 5 anion clusters, $V_n^-$, $Nb_n^-$, and $Ta_n^-$. For these elements, the threshold for anion cluster reactivity is significantly shifted from $n = 5$ to much larger sizes, with the abrupt rise in reactivity occurring only above $n = 14$–15. Possible reasons for the drastic difference in reactivity between the earlier and later transition metal anion clusters are discussed.

*Keywords:* Adsorption; Transition metal; Supersonic expansion

## 1. Introduction

Investigation of the interactions between transition metals, clusters or surfaces, and different adsorbed substances has been the focus of intensive studies for many years. The chemistry and the structure of transition metal clusters is of long standing interest because of their potential use as catalysts [1] which have numerous applications in technology and industry. Over the last 20 years such investigations provided considerable insights into the details of metal–adsorbate interactions, including reaction on metal surfaces. There have been many previous experimental [2–9], and theoretical studies [10–12] involving transition metal clusters and their reactivity with a large variety of small molecules, for example, nitrogen oxide, carbon monoxide, molecular hydrogen, oxygen and benzene. In spite of this lively interest, the detailed mechanism of their chemisorption on transition metal clusters is still poorly understood.

Cations and anions, as well as neutral clusters, of the transition elements are quite reactive towards many small molecules, and exhibit a very rich and complex chemistry. Transition metal clusters can nowadays easily be produced by modern techniques such as laser vaporization, and this permits in particular for ionic species convenient studies of their reactivity as a function of size, charge and type of metal. A considerable advantage of ions lies in the ease of their mass selection and trapping for extended periods of time under well-defined experimental conditions. Similar studies of neutral clusters are experimentally more difficult, but comparisons of the results for anionic and cationic clusters and, where available, for neutral clusters as well, suggest that the charge has only minor influence, and that in most cases the charged species exhibit very similar reaction channels as the corresponding neutrals [12]. The versatile laser vaporization source developed in our laboratory, coupled to our FT-ICR mass spectrometer allows us to generate clusters, both cationic and anionic of just about any material, and to study their reactions under well-defined conditions [4].

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The main goal of the work reported in this manuscript was to investigate the metal clusters of the group 5 (V, Nb, Ta) as well as of the later transition elements, group 9 (Co, Rh, Ir), and to assess the effect of their charge, and of the relative importance of electronic versus geometric effects. Although atoms and small molecules react readily with transition metal clusters in ways that are similar to the chemisorption reaction observed on the corresponding extended metal surface, one often observes cluster size dependent fluctuations in the rates and mechanisms of cluster–molecule reactions. Based on such results it was concluded that these species cannot be viewed simply as small pieces of bulk metal, but that they are rather distinct species whose structure and properties may change dramatically from one size to the next [12], and may also be critically dependent on the charge state.

Previous experimental studies of our group [4] have found considerable differences between the reactions of transition metal clusters, $Nb_n{}^{\pm}$ and $Rh_n{}^{\pm}$ with benzene, and their dependence upon cluster size and charge. Since the reaction mechanisms of benzene involving adsorption and dehydrogenation can be quite complicated, substituting a smaller, simple molecule like CO for the benzene should help to reduce the complexity and provide additional insights. Numerous theoretical and experimental studies involving CO as the probe reactant to investigate the chemistry of transition metal clusters have already been reported [13–15]. In general it is assumed in most of these studies that there should be no fundamental differences between the bonding of a CO molecule to a bulk metal surface and to a small metal cluster. Unlike in the case of benzene, in the high vacuum, binary collision environment of the mass spectrometer only one reaction pathway is possible for CO, a stabilization of the $M_nCO^{\pm}$ complex, most likely by radiation.

As already mentioned above, in the present paper we investigate the CO adsorption specifically on clusters of the transition metals of group 5, vanadium, niobium and tantalum, and group 9, cobalt, rhodium and iridium. We report here the reaction rates for these species based on the cluster size and charge, and suggest qualitative explanations for the observed reaction rates and trends.

## 2. Experimental details

The experiments were carried out on a modified FT-ICR mass spectrometer Bruker/Spectrospin CMS47X [16] equipped with a 4.7 T superconducting magnet, and a 60 mm × 60 mm cylindrical “infinity” cell. The instrument was fitted with an external ion source chamber for molecular beam sources. The transition metal cluster cations and anions were produced by pulsed laser vaporization [17,18] of a rotating metal disk using a focused 532 nm radiation of a Continuum Surelite II Nd:YAG laser (spot size on target about 500 μm), operating at 10 Hz with typically 12 mJ per 5 ns pulse. The plasma produced by the laser contained enough ions with no need for post-ionization. The vaporization was synchronized with a helium pulse (15 bar, 50 μs) from a home-built piezoelectric valve. The laser generated plasma entrained in the helium flowing through the confining channel (30 mm, 2 mm i.d.) was thermalized by collisions with the cold carrier gas, with further cooling and clustering occurring upon supersonic expansion into high vacuum. The cluster ions produced were accelerated downstream from a skimmer, transferred then into the high field region of the superconducting magnet, decelerated and trapped inside the ICR cell. This allows the storage of metal clusters for times ranging from milliseconds to minutes. If desired, the ions can be individually size selected, and their chemistry and reaction rates quantitatively studied under well-defined temperature and pressure conditions. Switching between cations and anions is simply accomplished by inverting the polarity of the transfer ion optic and of the trapping voltages.

To study the bimolecular cluster ion–molecule reactions the pressure inside the ICR cell was raised from the base value of around $1 \times 10^{-10}$ mbar to a constant pressure of typically $5.0 \times 10^{-9}$ mbar by controlled admission of the reactant gas carbon monoxide CO at room temperature. Commercially available CO (Messer-Griesheim, 99.997%) was used without further purification. Mass spectra were taken after varying reaction times. Relative rate constants for the first reaction step were obtained by fitting the observed time dependence of the parent and product cluster ion intensities assuming pseudo-first order kinetics, and converted into absolute rate constants.

In general, the reactivity of clusters depends on their translational and internal energies. The translational energy of the clusters is of the order of 1 eV, which converts into the center of mass frame of the reactants as 0.01–0.1 eV, depending on the mass of the cluster. Internally, the clusters are cooled below room temperature in the supersonic expansion. Overall, the conditions of the experiment are probably best described as near-thermal. Since the metal–CO interaction energy is of the order of 2 eV, the cluster is heated well beyond the initially near-thermal regime upon adsorption of CO.

## 3. Results

The anion and cation clusters of group 5 and group 9 transition metals were investigated under conditions of strictly bimolecular collisions, with a carbon monoxide pressure corresponding to a Langevin collision rate of about one collision per 15 s. The chemistry observed was quite simple, with essentially just one type of reaction being detected for all the species which were found to react at all, that is an attachment of CO to the cluster according to the equation:

$$M_n{}^{\pm} + CO \rightarrow M_n{}^{\pm}CO, \quad \text{with } M = V, Nb, Ta, Co, Rh, Ir$$

Obviously, the mass spectrometer cannot distinguish between a molecular CO adsorbed on the cluster, and CO dis-

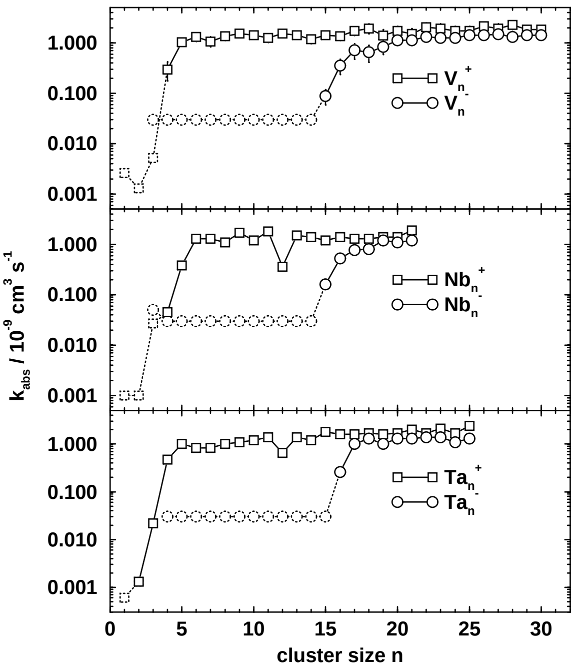

Fig. 1. Absolute rate constants of the adsorption of carbon monoxide CO on transition metal clusters of group 5, $V_n^{\pm}$, $Nb_n^{\pm}$ and $Ta_n^{\pm}$, $n = 1$–30 vs. cluster size $n$ and charge. Anions with $n < 3$ could not be produced because of the low electron affinities of small transition metal clusters. For cationic clusters, the reaction occurs even at small cluster sizes, $n = 2$ for tantalum, and $n = 4$ for vanadium and niobium, while for anionic clusters the first reaction product appears only for $n = 15$ and more. For $n > 20$, the reaction rate constants for both cations and anions are almost the same. Dotted symbols indicate the upper limit of the rate constant for apparently unreactive clusters.

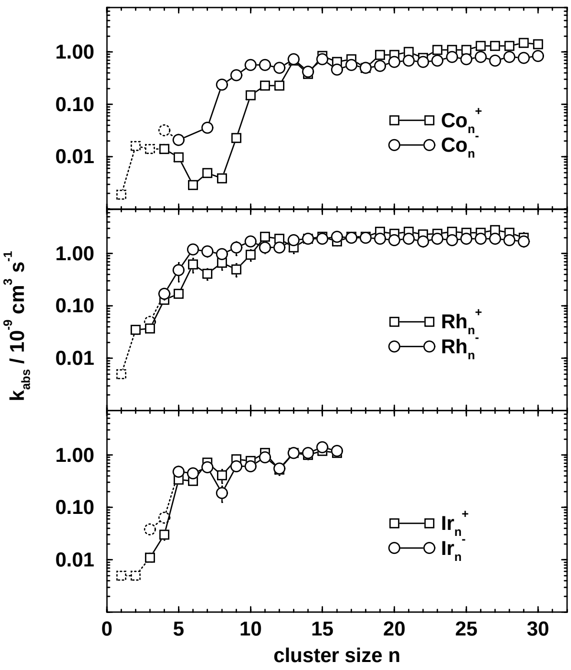

Fig. 2. Absolute rate constants of the adsorption of carbon monoxide CO on transition metal clusters of group 9, $Co_n^{\pm}$, $Rh_n^{\pm}$ and $Ir_n^{\pm}$, $n = 1$–30 as function of cluster size and charge. For cationic metal clusters, the adsorption of carbon monoxide can be observed for $n \geq 2$ for rhodium, $n \geq 3$ for iridium, and $n \geq 4$ for cobalt. The upper cluster size limit for iridium is lower due to the signal intensity distributed over the isotopes. The anions here adsorb CO at very small cluster sizes in contrast to group 5. For rhodium the first reaction product appears at $n \geq 4$ and for cobalt and iridium at $n \geq 5$. Dotted symbols indicate the upper limit of the rate constant for apparently unreactive clusters.

sociated into atoms. The results of our investigations and the measured rates are summarized graphically in Figs. 1 and 2. Already a cursory examination of the figures reveals that while both anions and cations of the group 5 elements, as well as the cations of group 9 exhibit a fairly similar behavior and trends, those of the anions of group 9 are drastically different. For the former, the small clusters up to $n = 2$–3 are essentially unreactive, but a rapid reactivity increase begins around $n = 3$–4. The rates increase by at least two orders of magnitude, and reach then a relatively steady value around $n = 6$–7. Upon closer inspection, one finds that this seemingly constant rate increases slowly with cluster size, a behavior which cannot be explained by the simple Langevin model. We attribute this behavior to the finite geometrical size of the clusters, which obviously increases with the number of atoms. The larger the cluster, the larger its geometrical collision cross-section becomes, and this will increase the cross-section calculated from the point charge Langevin model. Consistent with this interpretation, we find that the largest rate constants exceed the calculated Langevin rate by more than a factor of three.

However, a few minor deviations from the above overall description are found. Thus, in the case of $Co_n^-$ and $Ir_n^-$ anions, the increase in reactivity occurs only starting with $n = 4$, and conversely, for the $Ir_n^+$ cations, already $n = 3$ exhibits some observable reactivity. Furthermore, in particular for the $Co_n^+$ cations, the reactivity rise is not monotonic and less steep than for the other species, so that the limiting, steady value of rate is only reached around $n = 10$–12. For some specific clusters one observes deviations from the overall smooth trend which appear to be outside the experimental error. Thus, for instance the $n = 12$ cation clusters of Nb and Ta, as well as clusters of Ir seem to display somewhat lowered reactivity.

The most apparent anomaly, however, is the quite different behavior of all the anion clusters of group 5, that is $V_n^-$, $Nb_n^-$, and $Ta_n^-$. Unlike for the other species, here the steep rise in reactivity does not start around $n = 4$, but with $n = 15$ (for Nb and V) or $n = 16$ (Ta). Again, above this value the reactivity increases very rapidly by over three orders of magnitude, so that above $n \approx 17$–18 there is very little difference between the reactivities of anions and cations.

## 4. Discussion

When CO molecules with room temperature velocity distribution collide with a metal cluster, the energy of the collision complex formed is obviously well above its dissociation energy, and unless some energy conversion takes place, it will dissociate in a single vibrational period, on the timescale of 1 ps. This is undoubtedly what happens for the monatomic ions, and the smallest clusters. For larger molecules, for instance benzene, it was observed [3,4,19] and theoretically described that a stabilization of an $MC_6H_6^+$ complex can take place [19]. In such a case an IVR, intramolecular vibrational redistribution, of the available energy among the vibrational modes of the ligands takes place. This results in a “sticky collision,” with the complex being sufficiently long lived so that it can be stabilized by radiation, or possibly by the following collision, before it can dissociate.

In the case of CO ligands such an IVR cannot take place, and therefore no stabilization of an $MCO^+$ product is observed. For larger $M_n^+$ species, however, the complex can be stabilized by redistributing its internal energy among the vibrational modes of the metal cluster, which raises its effective temperature. Such a “hot” complex can, of course, still dissociate, but the rate of the dissociation will depend upon the excess energy, and the number of accessible states. The number of vibrational degrees of freedom, density of electronic states, and the “heat capacity” of the cluster will increase rapidly with the size of the cluster, resulting in a rapid decrease in the rate and efficiency of dissociation. For cluster sizes with $n > 3$ the dissociation apparently becomes sufficiently slow, so that radiative stabilization starts to compete successfully with re-dissociation of the collision complex.

At this point, it might be useful to consider the binding mechanism between the CO molecule and transition metals. In general the nature of the adsorption bond formed between CO and transition metal clusters is usually explained by the interaction of the CO molecular orbitals with the metal d states, and charge transfer between the metal and the ligand [20]. A useful model for the CO–transition metal bond was introduced by Blyholder [21]. The carbon monoxide can be viewed in the same time as a $\sigma^*$ donor, $\pi$ donor and $\pi^*$ acceptor [11], with the bond arising through interaction of the orbitals of CO with the d-orbitals of the metal. Recent combined X-ray emission spectroscopy and density functional theory studies confirmed this view, and showed that extensive mixing of the metal bands with the CO molecular orbitals takes place [22]. This leads to a weakening of the internal CO $\pi$-bond and strengthening of the $\sigma$-bond, which is quite obvious since $\pi^*$-back-donation increases and $\sigma^*$-donation decreases electron density in an antibonding orbital of CO. In view of this model the relative position of the d-orbitals of the metal should be important, and this will surely change across the transition metal series. As one proceeds from left to right, the increasing $Z$-value and correspondingly increasing screened nuclear charge lead to stabilization of the d-orbitals. This effect is evident in the physical properties of group 5 and group 9 atoms and bulk surfaces summarized in Table 1. Ionization potential, electron affinity, electronegativity and work function are consistently significantly smaller for group 5 than for group 9 metals. Since clusters bridge the gap between the atom and the bulk, it seems justified to interpolate these values and conclude that the same trend holds true for the clusters studied here. The extra electron in anionic clusters of group 5 will be more weakly bound and more delocalized than in the corresponding species of group 9.

Table 1
Ionization potential, electron affinity, Allred–Rochow electronegativity and work function of groups 5 and 9 transition metals

| | IP (kJ/mol) | EA (kJ/mol) | EN | WF (eV) |
|---|---|---|---|---|
| Group 5 | | | | |
| V | 650 | 50 | 1.45 | 4.3 |
| Nb | 664 | 100 | 1.23 | 4.3 |
| Ta | 761 | 60 | 1.33 | 4.25 |
| Group 9 | | | | |
| Co | 758 | 70 | 1.70 | 5.0 |
| Rh | 720 | 120 | 1.45 | 4.98 |
| Ir | 880 | 160 | 1.55 | 5.3 |

It has previously been suggested, that important for the reactivity of clusters is the strength of the metal–ligand bond [13]. However, the available data suggest that the binding energies for the ions of all the transition metals studied here are relatively large. Since charge donation and back-donation are equally important, there is no obvious reason why the binding energies of the group 5 anions should be significantly smaller than those of the cations.

At least for neutral bulk surfaces, the binding energies of molecular CO vary relatively little across the transition metal series and are for most metals close to 2 eV. Those of the atomic components C and O, however, decrease substantially from left to right [23]. Thus, for instance, the binding energy of atomic oxygen decreases from some 8 eV for Nb to about 4 eV for Pd [24]. Accordingly, CO tends to adsorb dissociatively on group 5 metals, but in molecular form on metals of group 9. However, as we have mentioned previously, based on mass spectrometry alone, one cannot determine unambiguously whether the carbon monoxide molecules are absorbed on the cluster in molecular form, or dissociated into atoms. Ligand exchange reactions or collision-induced dissociation might help to clarify this problem.

Since similar reactivity trends have been observed in reactions with benzene [4], a satisfying explanation has to account for both observations and should not rely on the particular population of bonding and antibonding orbitals in the metal–CO bond. One possible reason of the observed difference between group 5 and group 9 might lie in the d-orbital stabilization discussed above. In the case of cations, the removal of the electron results in further lowering of the d-orbital, and facilitates the initial adsorption of the CO on the positively charged cluster surface, in both groups 5 and 9. When an electron is added to the neutral cluster, the longer-lived complex formation is still possible for group 9 anions, while the presence of an additional electron in the higher lying d-orbitals of the group 5, and the increased negative charge may interfere with the formation of a longer-lived collision complex. An elastic collision occurs on a picosecond timescale, without any IVR or other inelastic processes taking place. One can imagine that the largely delocalized extra electron extends the geometric boundaries of the cluster. Recent ion mobility experiments of cationic and anionic gold clusters have clearly shown that in fact anionic clusters are bigger than cationic ones [25,26].

The CO molecule is elastically repelled before it gets close enough to form a chemical bond, simply because the electron cloud formed by the excess negative charge is too big. Only when the cluster gets sufficiently large, that is more than 15–16 metal atoms, is the effect of the negative charge sufficiently reduced, so that binding of CO can take place. It should be noted, that up to about 10–13 atoms, most of the atoms of the cluster will be on its surface. Only beyond this limit at least a few atoms will be in the cluster interior. In group 9 clusters with their higher electron affinity, the extra electron is more confined, and formation of chemical bonds is not obstructed. We believe that this stabilization of the d-orbitals from group 5 to group 9 may be the reason for the dramatic difference observed between the behavior of the anionic clusters of the two groups, in reactions with CO as well as with benzene.

## 5. Conclusions

The cluster size and charge state dependence of the reactivity of group 5 and group 9 transition metal clusters towards CO under binary collision conditions have been investigated. While larger clusters react and adsorb CO with relatively uniform, probably collision rate limited efficiency, for the smallest clusters no reactions were detected. A puzzling observation is that while for cations of both groups 5 and 9 as well as for anions of group 9 a steep onset of reactivity occurs around $n = 4$, for the anions of group 5 this onset is shifted to about $n = 15$. This drastically different behavior between the anions of groups 5 and 9 is tentatively attributed to the increased screened nuclear charge and stabilization of the group 9 d-orbitals.

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