H_2 Adsorption on 3d Transition Metal Clusters: A Combined Infrared Spectroscopy and Density Functional Study

Ingmar Swart,[†] Frank M. F. de Groot,*[,†] Bert M. Weckhuysen,[†] Philipp Gruene,[‡] Gerard Meijer,[‡] and André Fielicke*[,‡]

Inorganic Chemistry and Catalysis Group, Department of Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, the Netherlands, and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

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The adsorption of H_2 on a series of gas-phase transition metal (scandium, vanadium, iron, cobalt, and nickel) clusters containing up to 20 metal atoms is studied using IR-multiple photon dissociation spectroscopy complemented with density functional theory based calculations. Comparison of the experimental and calculated spectra gives information on hydrogen-bonding geometries. The adsorption of H_2 is found to be exclusively dissociative on Sc_nO^+, V_n^+, Fe_n^+, and Co_n^+, and both atomic and molecularly chemisorbed hydrogen is present in $Ni_nH_m^+$ complexes. It is shown that hydrogen adsorption geometries depend on the elemental composition as well as on the cluster size and that the adsorption sites are different for clusters and extended surfaces. In contrast to what is observed for extended metal surfaces, where hydrogen has a preference for high coordination sites, hydrogen can be both 2- or 3-fold coordinated to cationic metal clusters.

I. Introduction

The interaction of H_2 with transition metals is of fundamental interest to the fields of hydrogen storage, catalysis, and metallurgy. Especially the adsorption of hydrogen on nickel, cobalt and iron is of considerable importance as these metals are active hydrogenation (nickel), ammonia synthesis (iron), or Fischer−Tropsch (cobalt and iron) catalysts. Under reaction conditions, the surface of catalytically active metals is often covered with hydrogen. By studying H_2 adsorption on small transition metal clusters, one can obtain fundamental insight into elementary steps that take place on catalytically active surfaces.

Hydrogen adsorption on transition metal clusters has been studied extensively and has been summarized in two reviews.[1,2] However, structural information on the hydrogen binding sites is relatively scarce. On extended metal surfaces hydrogen is known to have a preference for high coordination sites. However, it is not at all clear if this is also the case for hydrogen adsorption on transition metal clusters that contain only a few metal atoms. To date, only indirect information on bonding geometries is available from hydrogen uptake measurements. It is generally accepted that H_2 dissociates upon adsorption on transition metal clusters. Experimental evidence in support of this mechanism includes the observation that the ionization potential of metal clusters increases upon adsorption of hydrogen,[3] the strength of the cluster−hydrogen bond[4−8] and that the reaction between hydrogen and metal clusters is irreversible at room temperature.[9] From these and other experiments it has been concluded that hydrogen can be 2-, 3-, or 4-fold coordinated to metal clusters, but not linearly.

Upon exposure of the transition metal clusters to H_2, the clusters bind H_2 molecules and form metal hydride complexes. Reactivity studies have demonstrated that the reactivity of different transition metals toward H_2 shows large variations with cluster size. The reactivity of a cluster is found to correlate with its electronic properties, as expressed, for instance, by the HOMO to LUMO excitation energy or by an (effective) ionization potential of the cluster. It has been argued, therefore, that the chemisorption probability depends on the energy barrier caused by Pauli repulsion between H_2 and the metal cluster. For the reaction of niobium clusters with H_2 it has been found that the entrance channel barrier is determined by an avoided crossing with ionic potential surfaces. More generally, the requirement for a charge transfer in the activation of H_2 could account for the dependence of the reaction rate on the ionization potential.[10−12] At sufficiently high H_2 concentration the cluster usually saturates with a well-defined number of H_2 molecules. So far, this element specific saturation behavior for the reaction with hydrogen has been studied, e.g., for vanadium, iron, and cobalt clusters.[13−15] These saturated complexes can be considered as ideal model systems for the above-mentioned highly covered surfaces in hydrogenation reactions. To date, there are no conclusive explanations for the observed saturation stoichiometries, e.g., in terms of cluster structure or H adsorption geometry. A systematic study on hydrogen saturated transition metal clusters that allows for an understanding of the interaction between metal and hydrogen ligands is thus highly desirable. By performing this study on a series of 3d transition metals, one can gain insight into the effect of increasing d-orbital occupation.

Few studies on scandium clusters containing more than 3 metal atoms have been reported in the literature. The ionization potentials of scandium monoxide clusters, Sc_nO^+, have been measured[16] and the magnetic moments of neutral scandium clusters containing between 5 and 20 metal atoms have been determined.[17] The structures of bare scandium clusters have been calculated using density functional theory (DFT).[18] However,

* Corresponding authors. E-mail: F.M.F.d.G., f.m.f.degroot@uu.nl; A.F., fielicke@fhi-berlin.mpg.de.
[†] Utrecht University.
[‡] Fritz-Haber-Institut der Max-Planck-Gesellschaft.

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to the best of our knowledge, no studies on H_2 or D_2 chemisorption on scandium clusters have been performed.

In contrast to this, vanadium clusters have received considerable research interest. The adsorption of H_2 and D_2 has been studied using flow tube and ion trap techniques.[4,13,19−23] The V_n^+−D bond energies have been measured by studying the kinetic energy dependence of the reaction of cationic vanadium clusters with D_2. These bond energies have been determined to be between 2 and 3 eV, depending on cluster size. From these and other studies it has been proposed that H_2 and D_2 bind dissociatively to vanadium clusters, which has been confirmed by a combined vibrational spectroscopy and DFT study on hydrogen saturated cationic vanadium clusters.[13]

The reaction of H_2/D_2 with iron clusters has been the subject of several studies as well. The reactivity of iron clusters toward H_2 has been found to depend strongly on the size of the cluster[24] and to correlate with the difference between ionization potential and electron affinity of the clusters. The Fe_n^+−D bond energies have been measured for clusters with $n = 2-15$, and vary from 1.4 to 2.8 eV.[6] From magnetic deflection experiments it has been found that the magnetic moment of iron clusters increases upon hydrogen chemisorption.[25] For Fe_n clusters it has also been shown that the ionization potential increases upon hydrogen adsorption.[3] Vibrational spectra of neutral iron hydride complexes have been measured using a tunable CO_2 laser covering the spectral range from 885 to 1090 cm^{-1}. Several absorption features, ascribed to Fe−H modes, have been observed in this spectral range.[26] DFT calculations on $Fe_{13}H_{14}$ (T_d symmetry) indicate that 2- and 3-fold coordinated hydrogen atoms give rise to vibrations in the 820−1500 cm^{-1} range. The vibrational spectrum of FeH_2 in the gas-phase[27] shows that the antisymmetric stretch mode has a frequency of 1674 cm^{-1}.

The reaction of H_2/D_2 with cobalt clusters is among the most intensively studied reactions in the field of cluster science. As in the case of iron clusters, the reactivity of cobalt clusters toward H_2/D_2 is found to be strongly size dependent.[10,28] The reactivity does not strongly depend on temperature,[29] indicating that the adsorption of hydrogen on cobalt clusters is a nonactivated process. The experimentally determined Co_n^+−D bond energies do not strongly depend on size (for clusters with $n = 2-16$) and generally increase with increasing cluster size from 2 to 2.6 eV. Indirect information on deuterium binding sites is available from D_2 uptake measurements.[30] Hydrogen is believed to be 2-, 3-, or 4-fold coordinated to cobalt, but never linearly.

As nickel is an effective hydrogenation catalyst, the reaction of H_2/D_2 with nickel clusters has also received considerable interest. Again, the reaction of small nickel clusters with hydrogen depends on the size of the cluster.[8] Nickel clusters have been found to bind more H_2 molecules than other transition metal clusters,[31] suggesting that part of the adsorbed hydrogen is bound in a different way to nickel than to other transition metals. The Ni_n^+−D bond energies[8] have been found to be very similar to the V_n^+−D, Fe_n^+−D, and Co_n^+−D bond energies. The bond strength increases from 2 eV for the trimer to 2.6 eV for a cluster containing 16 nickel atoms. The values for the larger clusters are very close to the values obtained for hydrogen adsorption on extended surfaces. The similarity in bond strengths for the different transition metals suggests that the metal d-orbitals do not play an important role in the M−H bond. One can, therefore, expect that the metal hydrogen vibrations have similar frequencies.

Vibrational spectroscopy, combined with quantum chemical calculations can provide detailed information on adsorption geometries for cluster complexes.[13,32] This article focuses on the determination of the size dependent hydrogen adsorption sites, at high (saturation) hydrogen coverage, on Sc_nO^+, V_n^+, Fe_n^+, Co_n^+, and Ni_n^+ clusters with $n = 3-20$. Vibrational spectra of the transition metal hydride complexes have been obtained using infrared multiple photon dissociation (IR-MPD) spectroscopy. Vibrational spectra have been measured in the range from 500 to 1600 cm^{-1}, covering both the M−H stretch, ν(M−H), and deformation mode, δ(M−H), region. Vibrations of the metal cluster core are expected to be clearly below 500 cm^{-1}.[33,34] For the nickel deuteride complexes, the spectral region in which the D−D stretch, ν(D−D), vibration is expected, has been scanned as well. The very high H/Ni ratios reported in the literature would indicate partly molecularly bound H_2 and vibrational spectroscopy can unambiguously resolve how H_2/D_2 is bound to nickel clusters. The experimental work is complemented with density functional theory calculations for complexes containing 4, 5, and 6 metal atoms. Comparison of the experimental and calculated spectra provides information on hydrogen adsorption geometries and bond strengths.

II. Experimental Methods

The experiments have been performed using a molecular beam machine coupled to a beamline of the Free Electron Laser for Infrared eXperiments, FELIX,[35] at the FOM Institute for Plasma Physics in Nieuwegein, The Netherlands. The setup and details of the measurement procedure have been discussed in detail before.[13,32,36] Metal clusters are produced by pulsed laser ablation using the second harmonic output of a Nd:YAG laser and subsequent condensation in a flow of He. Neutral, anionic and cationic clusters are produced in this process. In this study we only report on the hydrogen adsorption on cationic metal clusters. Downstream of the cluster source the clusters enter a flow reactor channel where they can react with H_2 that is injected by a pulsed valve. The extent of complex formation is controlled by adjusting the gas flow through the valve. Upon increasing the H_2 content in the reactor channel, sequential H_2 molecules are adsorbed on the metal clusters. The H_2 partial pressure in the reactor channel is increased until no more H_2 molecules are adsorbed, i.e., until the clusters are saturated with hydrogen. After reacting with H_2, the molecular beam is expanded into vacuum and shaped by a skimmer and an aperture, before entering the extraction region of a time-of-flight mass spectrometer. A counter-propagating pulsed IR beam delivered by FELIX is directed trough the aperture to ensure that the full cross-section of the molecular beam is exposed to the IR radiation. When the IR radiation is resonant with an IR-allowed transition of the cluster complex, sequential absorption of single photons can take place. The photon energy is quickly transferred to the heat bath of other modes via internal vibrational redistribution such that subsequent absorption of other photons is possible on the same transition. This process is facilitated by the high density of vibrational states.[37] In principle, relaxation can occur by emitting photons, electrons, or by fragmentation.[36] Electron emission and fragmentation lead to changes in the cluster distribution that can be probed using mass spectrometry. The dissociation energy of metal hydride and deuteride clusters is typically on the order of several electronvolts,[4−8,38] and hence many IR photons have to be absorbed to overcome the barrier to fragmentation. For example, the binding energy of H_2 on V_5^+ is 2.4 ± 0.3 eV,[19] so for a cold cluster at a minimum 14 photons at 1400 cm^{-1} have to be absorbed to induce fragmentation. To observe fragmentation on the time scale of the experiment, the number of absorbed photons must be even

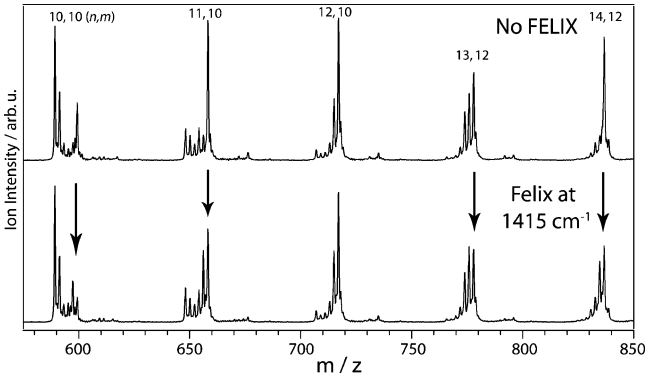

Figure 1. Mass spectra of fully hydrogen saturated $Co_nH_m^+$ complexes with mass/charge ratios between 570 and 850. The top spectrum shows part of the mass distribution of cluster complexes in the molecular beam where, e.g., 11,10 indicates the $Co_{11}H_{10}^+$ complex, etc. The lower mass spectrum shows the mass distribution upon overlap of the molecular beam with a beam of IR radiation resonant with an infrared active mode of the cluster complexes. The arrows indicate the mass peaks that are seen to undergo IR induced fragmentation.

higher. For the metal hydride complexes, fragmentation under loss of H_2 molecules is observed to be the dominant cooling process. This is illustrated in Figure 1 where significant fragmentation is observed for the $Co_{10}H_{10}^+$, $Co_{11}H_{10}^+$, $Co_{13}H_{12}^+$, and $Co_{14}H_{12}^+$ complexes upon irradiation with IR photons with a frequency of 1415 cm^{-1}, accompanied by the simultaneous growth of the ion intensities for the $Co_{10}H_8^+$, $Co_{11}H_8^+$, $Co_{13}H_{10}^+$, and $Co_{14}H_{10}^+$ complexes.

The mass spectrometer extraction pulse is timed such that spectra are recorded of a part of the cluster distribution that is exposed to a macro pulse of IR radiation (lower trace in Figure 1). Mass spectra of a reference distribution that is not exposed to IR radiation are recorded on alternate shots to compensate for long-term variations in the cluster intensities (upper trace in Figure 1). Tracking the intensity of certain complexes in the mass spectrum as a function of the IR frequency allows the construction of their IR-MPD spectra. Parts of the experiments have been repeated with D_2. However, apart from the expected shift of the vibrational frequencies due to the different reduced masses, no other changes are observed in the spectra. The spectra of nickel hydride complexes in the range of the hydrogen−hydrogen stretch vibration have been measured using deuterium for experimental reasons.

For scandium, vanadium, iron, and cobalt commercially available metal rods have been used as ablation targets. The study of H_2 chemisorption on nickel clusters is complicated by the natural isotopic distribution of nickel. Therefore we have worked with an isotopically enriched nickel target, prepared by electroplating ^{58}Ni (>99.8%) onto an Au substrate. Details of the plating process can be found in the Supporting Information.

III. Computational Methods

To further investigate the M−H vibrations and to determine the hydrogen-bonding geometries, DFT calculations have been performed on hydrogenated metal complexes with 4, 5, and 6 metal atoms using the TURBOMOLE quantum chemistry package.[39−41] The calculations employ the BP86 parametrization of the exchange correlation functional and a triple-ζ valence plus polarization (TZVP) basis set for all atoms.[42] It has been shown that this approach gives good agreement with experimental data.[13]

The number of structural isomers dramatically increases with increasing cluster size. Because structural information on both bare and hydrogenated metal clusters is scarce, calculations have only been performed on complexes containing 4, 5, and 6 metal atoms for which the number of possible geometric isomers is limited. The following computational procedure has been applied. First the geometries of several cluster complexes were optimized for each cluster size. Different metal cluster geometries were used and hydrogen atoms were placed both in 2- and 3-fold coordination sites. Two-fold coordinated hydrogen atoms will be referred to as bridge (μ_2) bonded hydrogen atoms and 3-fold coordinated hydrogen atoms will also be referred to as face (μ_3) bound atoms. For every geometric isomer, optimizations have been performed using different spin states. The optimization procedure has been conducted without any symmetry restrictions. After the optimization procedure the vibrational spectrum was calculated within the harmonic approximation. The calculated photon absorption cross sections were convoluted with Gaussians with a width of 20 cm^{-1} and converted into depletion spectra according to

$$I(\nu) = 10^{-\sigma(\nu)*P_{FEL}(\nu)/c}$$

with $\sigma(\nu)$ the calculated single photon cross-section at photon frequency ν and $P_{FEL}(\nu)$ the output power of the free electron laser at frequency ν. The constant c is introduced to obtain the best possible agreement with experiment. This approach assumes that the absorption of the first photon is rate determining in the IR-MPD process and leads to good agreement of the simulated spectra to the experimental ones. No scaling factor was applied to the calculated vibrational frequencies.

We note that in this process only a small portion of the configurational space is probed and it is possible that the actual structures are different from the structures identified by the calculations. In nearly all cases, several different structures are close in energy and theory might not be accurate enough to correctly predict the ground state structure. DFT based calculations on transition metal clusters present a real challenge due to the magnetic properties of such systems and the importance of spin−orbit coupling and correlation effects. Furthermore, adsorbate induced changes in the magnetic moments of transition metal clusters have been observed.[25,43] Also the presence of metastable species in the molecular beam cannot be completely ruled out. However, no indications for the presence of metastable species in these kinds of experiments have been found. The IR spectra of the complexes are sensitive to the geometry and the electronic state of the cluster complex and the energy differences between low energy isomers are typically on the order of 0.1−1 eV. In case a structure could not be assigned on the basis of energetic considerations alone, a structure has been assigned on the basis of the comparison of the calculated and experimental spectra.

IV. Results and Discussion

First the saturation compositions of the metal hydride complexes will be discussed. Subsequently the results for the smaller complexes containing 4, 5, and 6 metal atoms, for which calculations have been performed, will be presented. This will allow a direct comparison between clusters of different metals. Finally the larger complexes will be treated element by element.

A. Complex Composition. Nearly all clusters in the size range under investigation react with H_2. Only Fe_3^+ and Co_3^+ do not bind any hydrogen. Upon increasing the H_2 pressure in the reactor channel, the metal clusters sequentially bind H_2 molecules until a size specific saturation coverage is reached. For some of the Ni_n^+ clusters a product distribution is observed

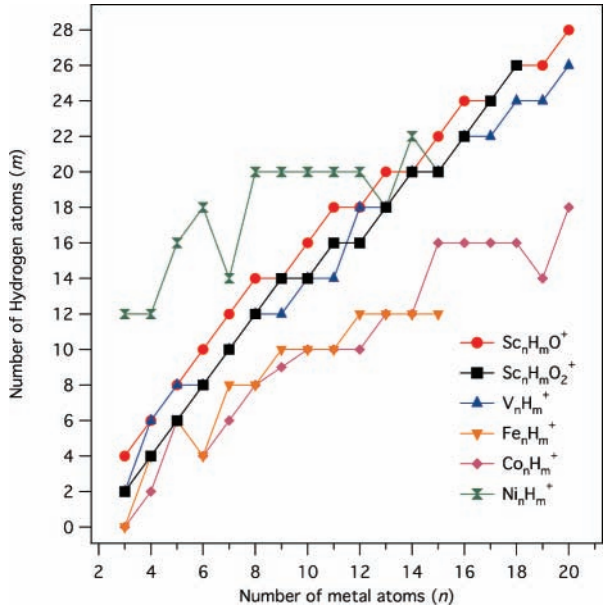

Figure 2. Largest number of hydrogen atoms present in $Sc_nH_mO^+$, $Sc_nH_mO_2^+$, $V_nH_m^+$, $Fe_nH_m^+$, $Co_nH_m^+$, and $Ni_nH_m^+$ complexes as a function of cluster size ($n = 3-20$). For several $Ni_nH_m^+$ complexes a distribution was observed but also in this case, the largest value of m is given.

in the mass spectrum even at the highest H_2 content used, indicating that saturation has not yet been reached. For cobalt, a saturation behavior has been observed but upon increasing the H_2 content further, the cluster added additional weaker bound H_2 molecules. Physisorption of molecular hydrogen at temperatures below 150 K has been observed before on neutral iron clusters.[26] The maximum number of H_2 molecules that could bind under our experimental conditions as a function of element and cluster size, is given in Figure 2. As expected, the number of hydrogen molecules depends on the metal and on the size of the cluster; it increases as the clusters become larger, and it decreases from scandium to vanadium to iron to cobalt but then sharply increases for nickel. All metal clusters bind an even number of hydrogen atoms, except for Co_9^+ that binds 9 hydrogen atoms. In view of the strong (4.52 eV) H−H bond, one would expect to observe only species containing an even number of hydrogen atoms. The Co_9^+−D bond energy has been reported to be $\sim 2.3 \pm 0.3$ eV, and chemisorption is, therefore, not expected to be exothermic enough to permit the ejection of one hydrogen atom. A possibility could be that this complex is formed via fragmentation of a larger cluster via, e.g., CoH loss.

The cationic scandium clusters produced in our setup always contain one or two oxygen atoms. It has not been possible to produce bare metal clusters. Both Sc_nO^+ and $Sc_nO_2^+$ readily react with H_2. In many cases $Sc_nO_2^+$ clusters bind one H_2 molecule less than Sc_nO^+ clusters. Clearly, the number of hydrogen atoms that can bind to a certain cluster is larger than the number of identical adsorption sites. Hydrogen must therefore be bound in different adsorption sites. DFT calculations on scandium complexes with 4, 5, and 6 metal atoms, see below, indicate that structures with internal hydrogen atoms are not formed and that all hydrogen atoms are located on the surface of the cluster.

In case of the vanadium clusters, there is a clear correspondence between the maximum number of H-atoms that can bind to a cluster and the number of facets of the metal cluster, suggesting that hydrogen is predominantly bound on the facets of the metal cluster. It has been shown that indeed hydrogen is predominantly 3-fold coordinated to cationic vanadium clusters.[13]

The composition of the saturated cationic iron-hydride complexes agrees in most cases with previously reported values for neutral iron-hydride complexes.[24,26] For Fe_{11}^+, Fe_{14}^+, and Fe_{15}^+ the maximum number of H_2 molecules that is found to bind to the cationic cluster is lower than to the corresponding neutral cluster.[24,26]

Cationic cobalt clusters containing between 6 and 9 metal atoms are particularly unreactive toward molecular hydrogen.[7,9,10] Only at relatively high H_2 concentrations, H_2 could be adsorbed onto these clusters. Co_9^+ presents a special case, as it is the only metal complex that binds an odd number of hydrogen atoms.

Nickel clusters can bind significantly more H_2 molecules than the other transition metal clusters. The large hydrogen uptake by small Ni_n^+ clusters has been reported before,[31] although the values we report here are even slightly higher. A Ni_4^+ cluster is predicted to have a (distorted) tetragonal shape,[44−46] and the Ni_5^+ cluster is expected to have a trigonal bipyramid structure.[45−47] These clusters bind 6 and 8 H_2 molecules, respectively. The number of adsorbed hydrogen atoms corresponds to the number of facets plus two times the number of Ni atoms, suggesting that all facets are covered by one hydrogen atom and that additionally each Ni atom binds one H_2 molecule. Quantum chemical calculations support this assignment and will be discussed below. Also the other nickel clusters bind more H atoms than their number of facets and bridge sites. This strongly suggests that also on the larger nickel clusters part of the H_2 is molecularly chemisorbed. The vibrational spectra of nickel deuteride complexes have been measured in the 2100−2700 cm^{-1} range to investigate this further.

B. Complexes with $n = 4-6$. Infrared multiple photon depletion spectra of metal hydride ($M_nH_m^+$) complexes with $n = 4-6$ are shown in Figure 3 (black) along with calculated linear IR absorption spectra (red) that are in best agreement with the experimental spectra. The corresponding cluster geometries are shown in Figure 4. Calculated vibrational spectra and optimized complex geometries of other isomers with 4, 5, and 6 metal atoms can be found in the Supporting Information.

Several element and size specific absorption features are identified in the 600−1500 cm^{-1} range. Vibrational spectra of bare cationic vanadium[33,34] and cobalt[48] clusters only show bands below 450 cm^{-1}, and we therefore assign the absorption bands in the 600−1500 cm^{-1} range to M−H vibrations.

The absorption bands of the scandium complexes are located at somewhat lower frequencies (<1200 cm^{-1}) compared to the other transition metal complexes. The spectra of $Sc_nH_mO^+$ do not change dramatically with cluster size. In all three cases the spectrum is dominated by an intense band centered at ~1100 cm^{-1}. For $Sc_5H_8O^+$ and $Sc_6H_{10}O^+$ this band has structure, implying the presence of multiple closely spaced bands. The vibrational spectrum of $Sc_4H_6O^+$ exhibits a narrow absorption band at 640 cm^{-1} that is absent in the spectra of $Sc_5H_8O^+$ and $Sc_6H_{10}O^+$. For the $Sc_5H_8O^+$ and $Sc_6H_{10}O^+$ complexes the vibrational spectrum of the lowest energy isomers are found to be in best agreement with the experimentally observed spectra. For $Sc_4H_6O^+$, the experimental spectrum is in best agreement with an isomer that is 0.03 eV higher in energy than the lowest energy isomer. This is within the expected accuracy of the calculations. The $Sc_nH_mO^+$ complexes are predicted to have the lowest possible spin state (doublet for $Sc_4H_6O^+$ and $Sc_6H_{10}O^+$- and singlet for $Sc_5H_8O^+$). The optimized cluster structure of $Sc_4H_6O^+$ shown in Figure 4 has C_{2v} symmetry, and the $Sc_5H_8O^+$

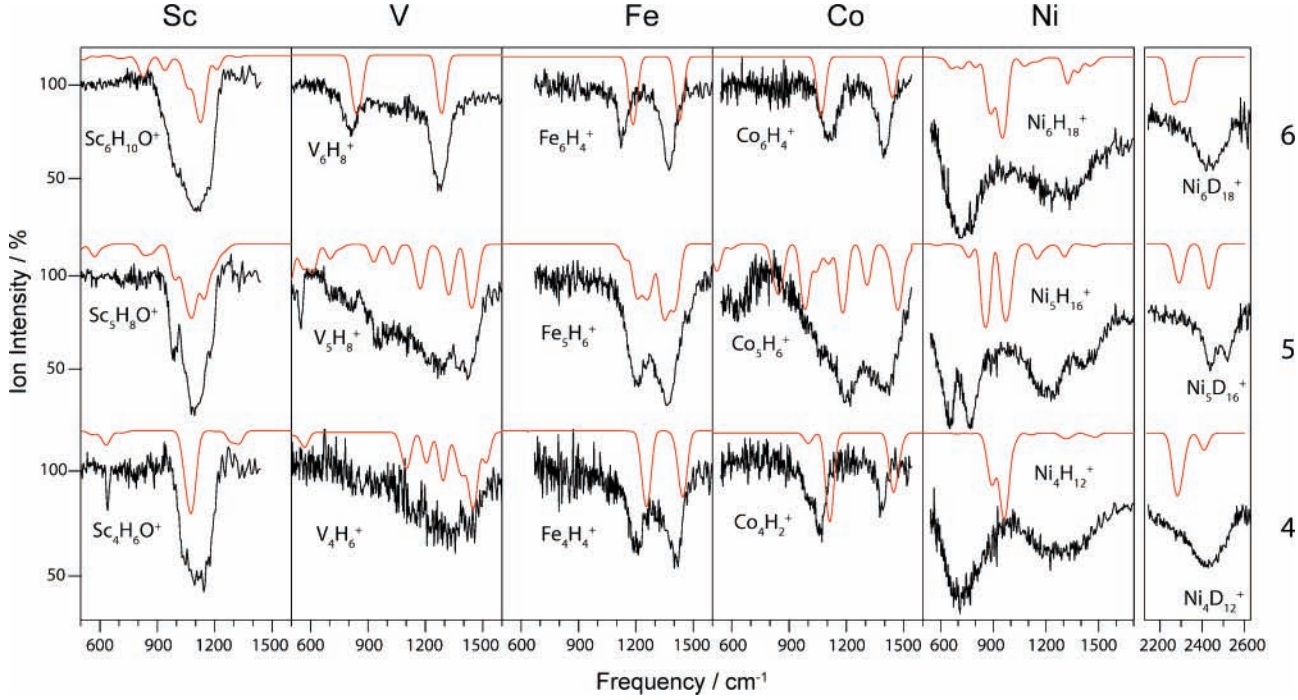

Figure 3. Experimental (black) and simulated (red) IR depletion spectra of hydrogen saturated $Sc_nH_mO^+$, $V_nH_m^+$, $Fe_nH_m^+$, $Co_nH_m^+$, $Ni_nH_m^+$, and $Ni_nD_m^+$ complexes for $n = 4$, 5, and 6 (bottom to top).

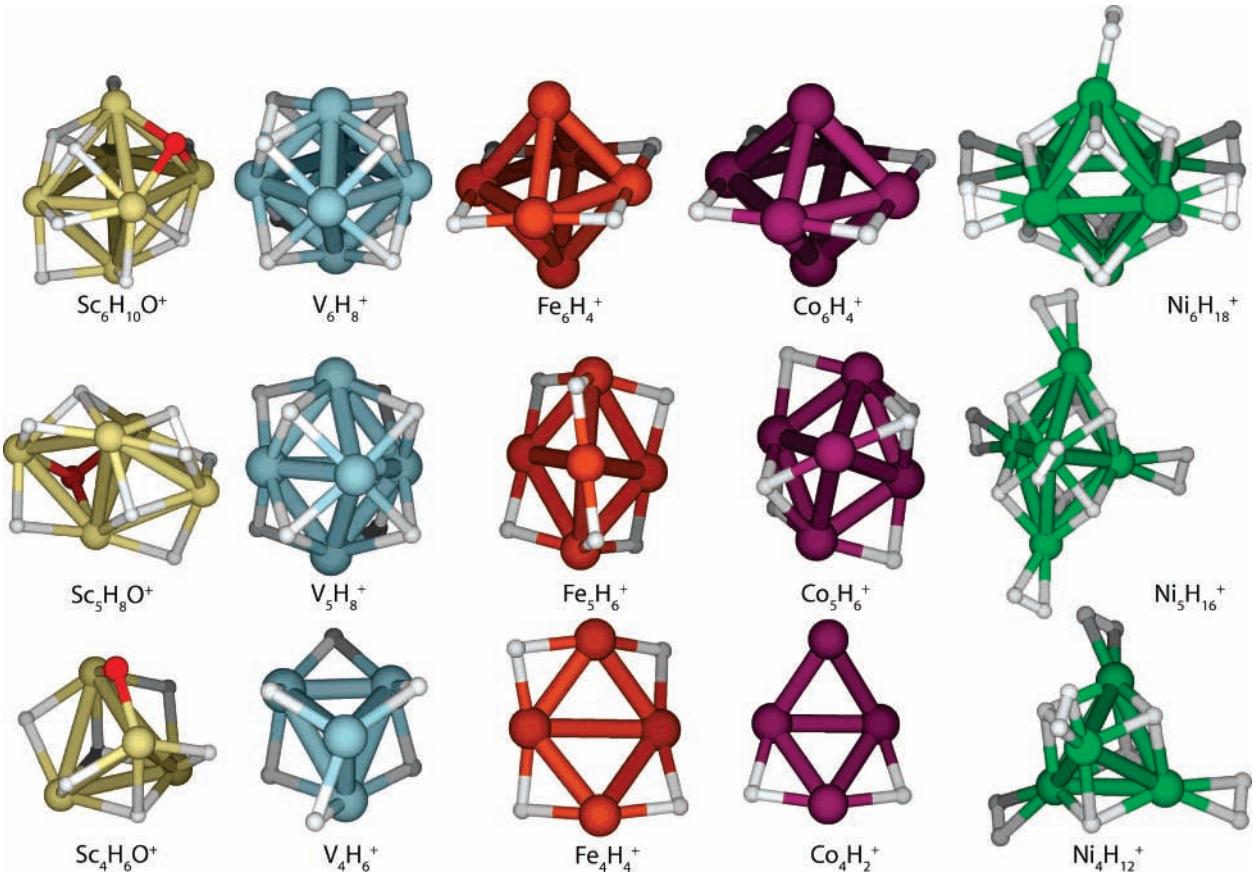

Figure 4. Optimized cluster geometries of $Sc_nH_mO^+$, $V_nH_m^+$, $Fe_nH_m^+$, $Co_nH_m^+$, and $Ni_nH_m^+$ (left to right) complexes for $n = 4-6$ selected on the basis of the comparison of experimental and calculated IR spectra.

and $Sc_6H_{10}O^+$ complexes have C_1 symmetry. For all three complexes a combination of bridge (μ_2) bound and face (μ_3) bound hydrogen atoms is predicted. The structure of the $Sc_4H_6O^+$ complex can be described as a tetrahedron spanned by the scandium atoms with four bridge (μ_2) bound and two face (μ_3) bound hydrogen atoms. The oxygen atom is bridge (μ_2) bonded. The five metal atoms in the $Sc_5H_8O^+$ complex span a distorted trigonal bipyramid, and the oxygen atom is face (μ_3) bound to the metal cluster. The structure of the $Sc_6H_{10}O^+$ complex can be described in similar terms. The six metal atoms form a distorted octahedron to which the oxygen atom is face (μ_3) bound. Isomers with hydrogen atoms inside

the metal cage are found to be at least 0.5 eV higher in energy than isomers with only surface bound hydrogen. Isomers with an internal oxygen atom are even less favorable, being at least 0.7 eV higher in energy than isomers with a surface bound O atom. Such species are therefore not expected to be present in the molecular beam. The calculations indicate that there are many closely spaced vibrations in the 900−1250 cm^{-1} range. The vibrations are not localized; i.e., they involve the collective motion of several hydrogen atoms and it is not straightforward to assign absorption bands to local modes. The most intense absorption band at ∼1100 cm^{-1} is assigned to collective stretch vibrations of bridge (μ_2) bonded hydrogen atoms. The fact that the band at 640 cm^{-1} is very narrow while all other absorption bands are much wider, suggests that this band is not due to a Sc−H vibration. The frequency of bridge (μ_2) bonded oxygen to scandium has been reported to be 615 cm^{-1}.[49] The calculations show that indeed the structure, whose vibrational spectrum is in best agreement with the experimental spectrum, contains a bridge (μ_2) bound O atom. Considering the agreement between experimental and calculated spectra, we tentatively assign the band at 640 cm^{-1} to a Sc−O stretch vibration of a bridge (μ_2) bound oxygen atom. The absence of this band in the spectra of $Sc_5H_8O^+$ and $Sc_6H_{10}O^+$ then suggests that the oxygen atom is 3-fold coordinated to scandium in these two complexes. Indeed, the calculations show that for these complexes the lowest energy isomers have a face (μ_3) bound oxygen atom.

Although H_2 is predominantly 3-fold coordinated to small cationic vanadium clusters, some 2-fold coordinated H can be present as well.[13] Several cluster size specific absorption bands are observed in the 550−1450 cm^{-1} range. In contrast to the spectra of $V_4H_6^+$ and $V_5H_8^+$, the spectrum of $V_6H_8^+$ consists of two well-resolved bands, indicating that this complex might have a higher degree of symmetry. Indeed, the calculations show that the lowest energy isomer has D_{4h} symmetry with only little deviation from octahedral symmetry and therefore a relatively simple vibrational spectrum. The hydrogen atoms bind on top of the facets of the octahedron formed by the vanadium atoms. The band centered at 1275 cm^{-1} can be assigned to a collective antisymmetric stretch mode of face bound (μ_3) H atoms. The band observed experimentally at 800 cm^{-1} corresponds to a collective bending mode of 3-fold coordinated (μ_3) hydrogen atoms. The $V_5H_8^+$ complex has C_{2v} symmetry, and the $V_4H_6^+$ complex only possesses C_1 symmetry. The $V_4H_6^+$ complex has a tetragonal core of vanadium atoms with all the hydrogen atoms bridge (μ_2) bound to the metal cluster. The structure of the $V_5H_8^+$ complex can be described as a slightly distorted structure of the $V_6H_8^+$ complex with one of the vanadium atoms removed. The experimental spectra are in best agreement with the calculated spectra of the lowest energy isomers. The calculated absorption band observed at 1450 cm^{-1} in the spectrum of $V_5H_8^+$ corresponds to a collective antisymmetric stretch vibration of bridge (μ_2) bound hydrogen atoms. The intense absorption band at 1280 cm^{-1} is due to the collective antisymmetric stretch vibration of the face (μ_3) bound hydrogen atoms.

The vibrational spectra of $Fe_4H_4^+$, $Fe_5H_6^+$, and $Fe_6H_4^+$ in the 700−1500 cm^{-1} range are very similar and consist of two well-resolved bands, implying that hydrogen is similarly bound in these three complexes and that these complexes have a relatively high degree of symmetry. The bands observed for the cationic iron hydride complexes are found at higher frequencies than reported earlier for neutral iron-hydride complexes.[26] Calculations on $Fe_{13}H_{14}$ reported in the literature assign these bands to bridge (μ_2) bound hydrogen atoms.[26] Indeed, the calculated complexes, whose vibrational spectra are in best agreement with the experimental spectra, contain only bridge (μ_2) bound hydrogen atoms. The isomers shown are 0.15, 0.14, and 0.08 eV higher in energy respectively than the lowest energy isomer. This is within the expected accuracy of such calculations, especially when considering different spin states. It is known that neutral iron hydride complexes have large magnetic moments.[25] Our calculations indicate that the cationic iron hydride complexes have a large number of unpaired electrons, 13 for $Fe_4H_4^+$, 17 for $Fe_5H_6^+$, and 19 for $Fe_6H_4^+$. In the $Fe_4H_4^+$ complex, the four iron atoms are arranged in a slightly bend rhombic shape with a hydrogen atom bound to each of the sides of the rhombus. It is interesting to note that for $Fe_4H_4^+$ and $Co_4H_2^+$ the calculations indicate that the four metal atoms are arranged in a distorted rhombus whereas for $Sc_4H_6O^+$ and $V_4H_6^+$ the metal atoms span a distorted tetrahedron. As observed for the scandium and vanadium complexes with five metal atoms, the five iron atoms of $Fe_5H_6^+$ span a trigonal bipyramid. The $Fe_6H_4^+$ complex has D_{4h} symmetry. The six iron atoms are arranged to form an octahedron with the four hydrogen atoms all bridge (μ_2) bound in one plane. The band with the lowest frequency (1200 cm^{-1} for $Fe_4H_4^+$, 1210 cm^{-1} for $Fe_5H_6^+$, 1130 cm^{-1} for $Fe_6H_4^+$) is assigned to the collective antisymmetric bending vibration of the bridge (μ_2) bound hydrogen atoms. The highest frequency band (1400 cm^{-1} for $Fe_4H_4^+$, 1360 cm^{-1} for $Fe_5H_6^+$, 1370 cm^{-1} for $Fe_6H_4^+$) is caused by the collective antisymmetric stretch vibration of the bridge (μ_2) bound hydrogen atoms.

Several cluster size dependent absorption bands are observed for the cobalt hydride complexes. The vibrational spectrum of $Fe_6H_4^+$ is very similar to the spectrum of $Co_6H_4^+$ suggesting that the hydrogen is similarly bound in these two complexes. The bands observed for $Co_6H_4^+$ (1110 and 1400 cm^{-1}) are shifted slightly compared to $Fe_6H_4^+$ (1130 and 1370 cm^{-1}). The spectrum of $Co_4H_2^+$ also resembles the spectrum of $Fe_4H_4^+$ except for the clear shoulder observed at 1000 cm^{-1} for $Co_4H_2^+$. However, the spectrum of $Co_5H_6^+$ shows some noticeable differences with the spectrum of $Fe_5H_6^+$. The vibrational spectra of the lowest energy isomers of $Co_4H_2^+$ and $Co_6H_4^+$ give good agreement with the experimental spectra of these species. The $Co_5H_6^+$ isomer that is in best agreement with experiment is 0.23 eV higher in energy than the lowest energy isomer. In case of $Co_5H_6^+$ two hydrogen atoms are 3-fold coordinated to the cobalt cluster with the other four bridge (μ_2) bonded. The agreement between the experimental and calculated spectrum of $Co_5H_6^+$ is not very good and it might well be that several isomers are present and/or that the actual structure is different from the one shown in Figure 4. The calculations indicate that the $Co_6H_4^+$ complex has the same structure as the $Fe_6H_4^+$ complex. It is predicted to have 13 unpaired electrons. The structure of the $Co_4H_2^+$ complex is very similar to the structure of $Fe_4H_4^+$ and has 9 unpaired electrons. The metal atoms form a slightly bend elongated rhombus with the two hydrogen atoms bridge (μ_2) bound symmetrically with respect to the long axis of the rhombus. Three bands (1390, 1060, and 1000 cm^{-1}) are observed in the vibrational spectrum of $Co_4H_2^+$ that are reproduced by the calculations. They can be assigned to collective antisymmetric stretch, symmetric bending, and antisymmetric bending vibrations of the bridge (μ_2) bound hydrogen atoms, respectively. The optimized geometry of $Co_4H_2^+$ is similar to the structure of the neutral complex reported in the literature.[50]

The IR-MPD spectra of $Ni_nH_m^+/Ni_nD_m^+$ ($n = 4-6$) are quite different from the other transition metal hydride complexes. For the nickel deuteride complexes bands located in the 2300−

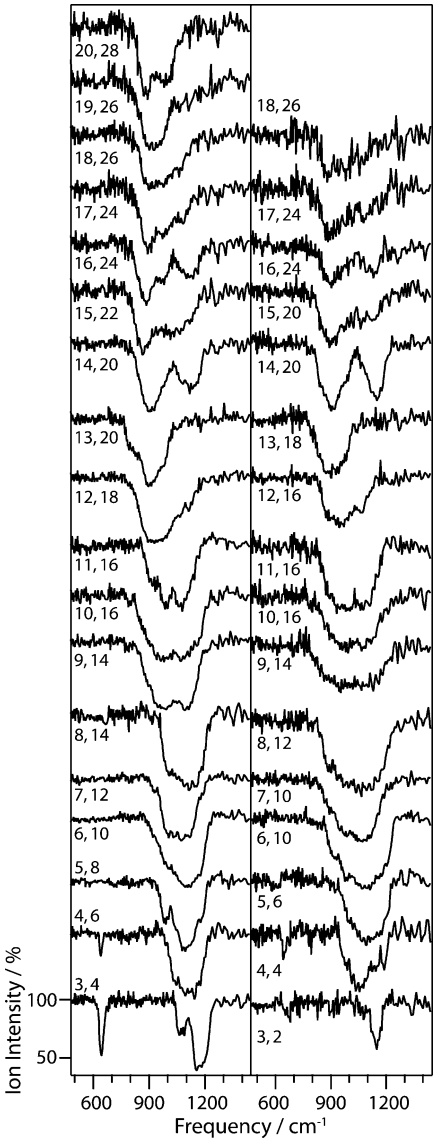

Figure 5. IR-MPD spectra of $Sc_nH_mO^+$ (left panel) for $n = 3-20$ and $Sc_nH_mO_2^+$ (right panel) for $n = 3-18$ (bottom to top). The values (n,m) correspond with the number of scandium and hydrogen atoms in the complex, respectively.

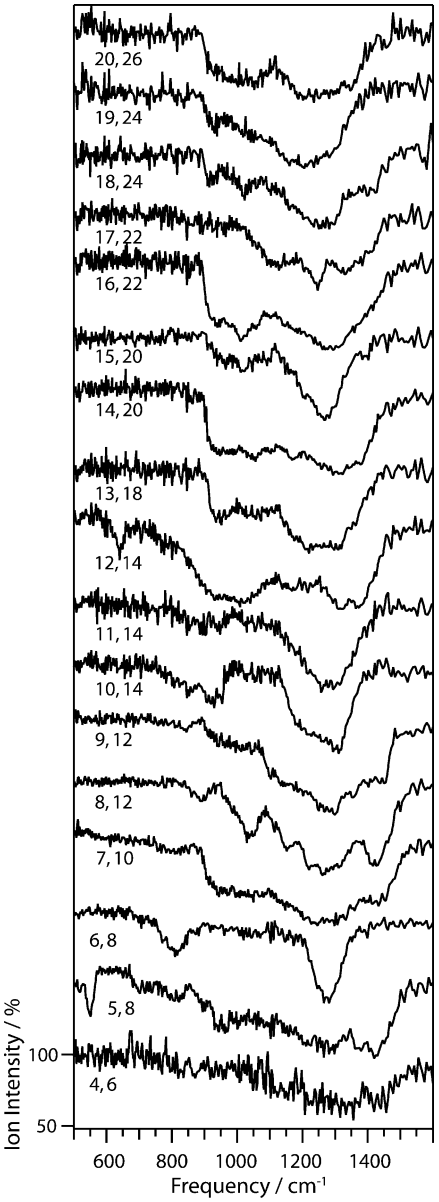

Figure 6. IR-MPD spectra of $V_nH_m^+$ complexes for $n = 4-20$ (bottom to top). The values (n, m) correspond to the number of vanadium and hydrogen atoms in the complex, respectively.

2500 cm^{-1} range are observed, proving that at least part of the D_2 is molecularly bound in these complexes. The frequency of the D−D stretch (ν(D−D)) band is shifted considerably to lower frequency compared to the frequency of free D_2 (2941 cm^{-1}). This implies that the D_2 molecules must be chemisorbed to the nickel cluster because physisorbed species only show small frequency shifts.[51] For $Ni_5D_{16}^+$ two relatively narrow bands are observed in the high-frequency range. The spectra of the nickel hydride complexes also exhibit distinctly different features in the low-frequency range compared to the other transition metal hydride complexes. A strong absorption band is observed for all nickel hydride complexes at frequencies below 900 cm^{-1}. The presence of these bands provides further evidence that (part of the) hydrogen is differently bound in nickel hydride complexes. They are assigned to the Ni−H_2 stretch (ν(Ni−H_2)) vibration. The metal−dihydrogen bond can be described by similar concepts used to describe the metal−olefin bond.[52] The H_2 molecule is virtually always side-on bonded to the metal. It can be described as a three-center-two-electron bond and is formed by donation of electron density from the occupied σ orbital of H_2 into an empty metal orbital of appropriate symmetry. The metal−dihydrogen bond is stabilized by back-donation of electrons from a (partially) filled metal *d* orbital to the σ^* orbital of H_2. The increased population of the antibonding σ^* orbital of H_2 weakens the H−H bond. The net effect is a transfer of electron density from H_2 to the metal. The bands in the 1000−1500 cm^{-1} range are also observed for the other transition metal hydride complexes and are assigned to stretch and deformation vibrations of bridge and/or face bound hydrogen atoms. The absorption bands in the spectra of $Ni_4H_{12}^+$ and $Ni_6H_{18}^+$ are much broader than for $Ni_5H_{16}^+$. This could be due to the presence of several isomers. A small rotational barrier for the chemisorbed H_2 molecules could also contribute to the broadening of the bands. For the $Ni_nH_m^+$ and $Ni_nD_m^+$ complexes the agreement between the experimental and calculated spectra is reasonable. All the experimentally observed features are reproduced by the calculations. Upon substitution of the hydrogen atoms by deuterium all modes, except for the Ni − Ni modes, scale down in frequency by a factor close to $2^{1/2}$ (±1.2%). The calculated frequencies of the ν(D−D) bands are too low, and the calculated frequencies of the ν(Ni−H_2)

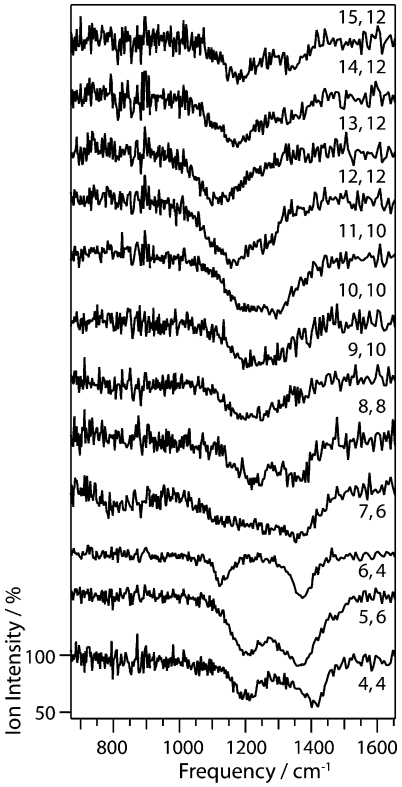

Figure 7. IR-MPD spectra of $Fe_nH_m^+$ complexes for $n = 4-15$ (bottom to top). The values (n, m) correspond to the number of iron and hydrogen atoms in the complex, respectively.

vibrations are too high. This demonstrates that our calculation overestimates the Ni−H_2 bond energy. All nickel complexes have the lowest possible (doublet) spin state. The quenching of the magnetic moment of nickel clusters upon adsorption of hydrogen has also been observed experimentally.[43] The $Ni_4H_{12}^+$ complex can be described as a cluster with a tetrahedral core spanned by the Ni atoms with one hydrogen atom bound to each facet of the tetrahedron and one H_2 molecule bound to each nickel atom. The structures of the $Ni_5H_{16}^+$ and $Ni_6D_{18}^+$ complex can be described in similar terms where the five nickel atoms in $Ni_5H_{16}^+$ span a trigonal bipyramid and the 6 Ni atoms in $Ni_6H_{18}^+$ span a tetragonal bipyramid.

C. Complexes with $n = 3 - 20$. ***1. Scandium.*** The experimental IR-MPD spectra of $Sc_nH_mO^+$ ($n = 3-20$) and $Sc_nH_mO_2^+$ ($n = 3-18$) are given in Figure 5. Several absorption features are identified in the 800−1250 cm^{-1} range. The spectra of $Sc_nH_mO^+$ and $Sc_nH_mO_2^+$complexes are very similar. This suggests that the Sc−H bonds are not significantly influenced by the presence of an additional oxygen atom. As outlined above, an oxygen atom bridge (μ_2) bound to scandium gives rise to an absorption band around 640 cm^{-1}. This band is only observed for $Sc_4H_6O^+$, $Sc_4H_4O_2^+$, $Sc_3H_4O^+$, and $Sc_3H_2O_2^+$, implying that the oxygen atom is 3-fold, or higher, coordinated to the other scandium complexes. As pointed out above, the lowest energy isomers of $Sc_5H_8O^+$ and $Sc_6H_{10}O^+$ contain a face (μ_3) bound oxygen atom. None of the $Sc_nH_mO^+$ spectra show any indication for high-symmetry structures. The most intense absorption band shifts to lower frequency with increasing cluster size.

The vibrational spectrum of tetrahedrally coordinated hydrogen in α-$ScH_{0.34}$ has been measured using neutron scattering. The frequencies of two modes associated with tetrahedrally coordinated hydrogen atoms were reported to be 834 and 1189 cm^{-1}, respectively.[53] For the largest cluster complex $Sc_{20}H_{28}O^+$ no band at ∼1200 cm^{-1} is observed, which indicates that $Sc_{20}H_{28}O^+$ does not contain any internal hydrogen atoms.

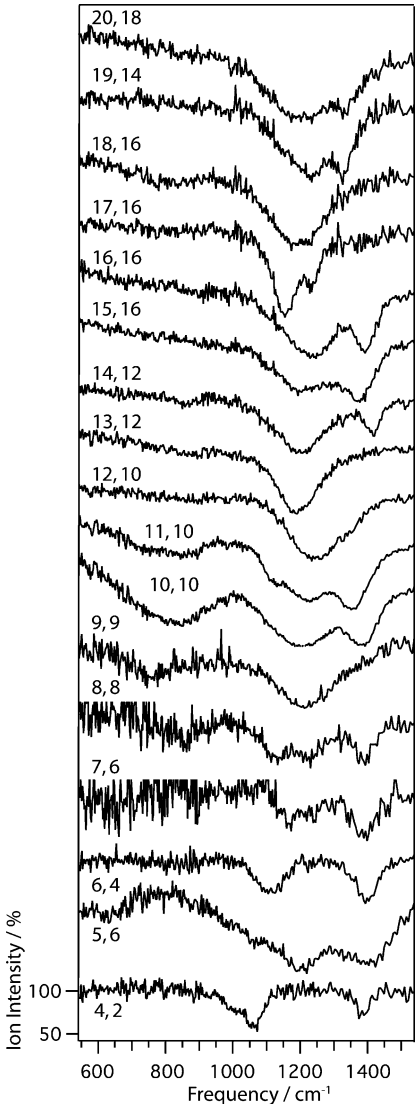

Figure 8. IR-MPD spectra of $Co_nH_m^+$ complexes for $n = 4-20$ (bottom to top). The values (n, m) correspond to the number of cobalt and hydrogen atoms in the complex, respectively.

2. Vanadium. The spectra of the hydrogen saturated vanadium clusters are given in Figure 6 for complexes containing between 4 and 20 metal atoms. Several cluster size specific absorption bands are observed in the 550−1450 cm^{-1} range. The spectra of most species show complicated band patterns, indicating that the vanadium hydride complexes do not have a high degree of symmetry. As described above, the nearly O_h symmetric $V_6H_8^+$ is an exception. The structures of $V_7H_{10}^+$, $V_8H_{12}^+$, and $V_9H_{12}^+$ have been discussed in the literature.[13] These complexes contain predominantly face (μ_3) bound hydrogen atoms, and also at least one bridge (μ_2) bound hydrogen atom. The experimentally observed band at ∼1400 cm^{-1} for these complexes is due the stretch vibration of bridge (μ_2) bound hydrogen atoms. The vibrational spectra of clusters containing 4, 5, 7−9, 12, 14, and 16−18 vanadium atoms all show an absorption band at ∼1400 cm^{-1}, and these complexes therefore likely contain some bridge (μ_2) bound hydrogen atoms.

3. Iron. The experimental IR-MPD spectra of $Fe_nH_m^+$ complexes with $n = 4-15$ are shown in Figure 7. For $Fe_4H_4^+$, $Fe_5H_6^+$, and $Fe_6H_4^+$ it has been shown above that the bands at ∼1400 and ∼1200 cm^{-1} are due to collective stretching and

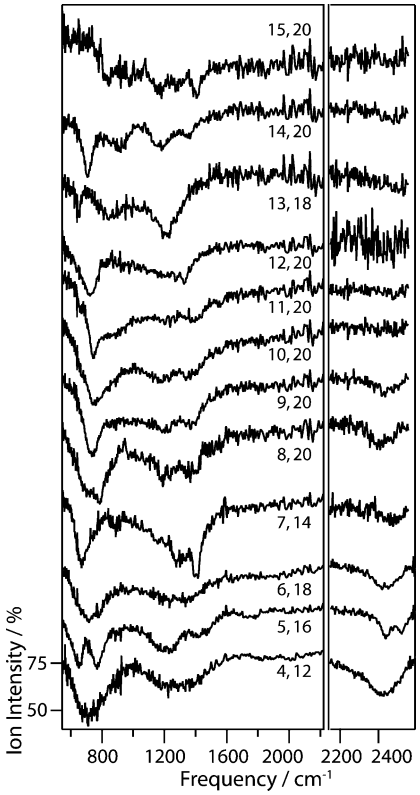

Figure 9. IR-MPD spectra of $Ni_nH_m^+$ complexes for $n = 4-15$ (bottom to top). The values (n, m) correspond to the number of nickel and hydrogen atoms in the complex, respectively.

bending vibrations of bridge (μ_2) bonded hydrogen atoms, respectively. The exact positions and spacing of these bands depend on the particular complex. Bands indicative of bridge (μ_2) bound hydrogen atoms are also present in the vibrational spectra of $Fe_7H_6^+$, $Fe_8H_8^+$, and $Fe_{15}H_{12}^+$. Calculations on $Fe_4H_4^+$, $Fe_5H_6^+$, and $Fe_6H_4^+$ containing face (μ_3) bound hydrogen atoms (see Supporting Information), show that the collective stretch vibration of 3-fold coordinated hydrogen atoms lies in the 1200−1300 cm^{-1} frequency range. Absorption bands at higher frequencies are clear indications for bridge (μ_2) bound hydrogen atoms. Part of the hydrogen is therefore expected to be bridge (μ_2) bound in $Fe_7H_6^+$, $Fe_8H_8^+$, $Fe_{14}H_{12}^+$, and $Fe_{15}H_{12}^+$. The presence of face (μ_3) bound hydrogen atoms cannot be excluded. Additional quantum chemical calculations are required to verify how hydrogen is bound in the larger complexes. It is interesting to note the difference between the spectra of $Fe_{12}H_{12}^+$ and $Fe_{13}H_{12}^+$. Both Fe_{12}^+ and Fe_{13}^+ bind 12 hydrogen atoms but the spectra of the hydride complexes are different. Therefore the hydrogen adsorption sites have to be different, which in turn implies a different metal cluster structure. DFT calculations have indeed predicted that the Fe_{12} cluster does not have icosahedral symmetry whereas the Fe_{13} cluster does.[54]

It is known from low-energy electron diffraction (LEED) studies that H atoms adsorbed on a Fe(110) surface are bound in quasi 3-fold hollow sites.[55] As outlined above, part of the hydrogen atoms are bridge (μ_2) bonded to cationic iron clusters. Apparently the bulk adsorption behavior has not yet been reached for iron clusters containing 15 atoms.

4. Cobalt. The experimental IR-MPD spectra of H_2 saturated cobalt complexes containing between 4 and 20 cobalt atoms are shown in Figure 8. The vibrational spectra of the cobalt hydride complexes change considerably as a function of cluster size. In the vibrational spectra of most complexes at least two bands are present in the 1050−1450 cm^{-1} range. The absolute and relative spectral positions depend on the number of metal atoms in the cluster. As described above, comparison of the experimental and calculated vibrational spectra of $Co_4H_2^+$, $Co_5H_6^+$, and $Co_6H_4^+$ indicates that for these complexes bands in the 1060−1110 and 1380−1410 cm^{-1} ranges are due to bridge (μ_2) bound hydrogen atoms. An absorption band with a frequency of ~1400 cm^{-1} is present in the spectra of several of the larger cobalt hydride complexes, implying that part of the hydrogen atoms are bridge (μ_2) bonded in those complexes. Hydrogen is known to adsorb in 3-fold hollow (μ_3) sites on a Co $(10\bar{1}0)$ surface.[56] Vibrational spectra of these species measured with HREELS[56] show adsorption features around 1150 cm^{-1}. Calculations on $Co_4H_2^+$, $Co_5H_4^+$, and $Co_6H_4^+$ that contain face (μ_3) bonded hydrogen atoms show that the stretch vibration of 3-fold coordinated hydrogen atoms lies in the 1200−1320 cm^{-1} range. Absorption bands in the 1100−1300 cm^{-1} range are present in the spectra of most cobalt hydride complexes. This strongly suggests that part of the hydrogen atoms are face (μ_3) bound in cobalt hydride complexes that have an absorption band in this range.

Interestingly, the vibrational spectra of $Co_{16}H_{16}^+$ and $Co_{17}H_{16}^+$ are rather different, suggesting that bulk adsorption behavior is not yet been reached for cobalt clusters with more than 17 metal atoms. For several complexes ($Co_5H_6^+$, $Co_8H_8^+$, $Co_9H_9^+$, $Co_{10}H_{10}^+$, $Co_{11}H_{10}^+$, and $Co_{18}H_{16}^+$) a broad band is observed at lower frequency. Such a broad band is not present in the vibrational spectra of the hydrogen complexes of the earlier transition metals. Considering the rather poor agreement between the experimental and the calculated spectrum of $Co_5H_6^+$, we cannot definitely assign this band.

5. Nickel. The IR-MPD spectra of $Ni_nH_m^+/Ni_nD_m^+$ complexes with $n = 4-15$ are shown in Figure 9. The spectra of most complexes are remarkably similar. A ν(D−D) band is observed for clusters up to $Ni_9D_{20}^+$. In the low-frequency range, there is an intense absorption band at ~750 cm^{-1} in the spectra of all complexes (except for $Ni_{15}H_{20}^+$) and (at least) two bands in the 800−1600 cm^{-1} range. As outlined above, the DFT calculations assign the band at 750 cm^{-1} to a ν(Ni−H_2) vibration. However, the disappearance of the other tell-tale feature of molecularly chemisorbed H_2, the ν(D−D) band, for clusters with 10 or more nickel atoms could indicate that only atomically bound hydrogen is present for the bigger complexes. Other possible reasons include a shift of the D−D stretch vibration to higher/lower frequency or that the D−D stretch vibrations have only little intensity. If the intramolecular axis

TABLE 1: Experimental Vibrational Frequencies (cm^{-1}) and Their Assignments for the $Sc_nH_mO^+$, $V_nH_m^+$, $Fe_nH_m^+$, $Co_nH_m^+$, and $Ni_nH_m^+$ Complexes

mode	Sc	V	Fe	Co	Ni
ν(M−H_2)					650−760
ν(D−D)					2420−2515
ν(M−μ_2H)	1100−1110	1420−1430	1350−1400	1385−1400	
ν(M−μ_3H)		1270−1280		1150−1230	1210−1270
δ(M−μ_2H)			1130−1220	1030−1110	
δ(M−μ_3H)		810			

of H_2 molecularly chemisorbed on an extended surface is parallel to that surface, the H−H stretch vibration will only have very little intensity due to the induced dipole in the metal. Considering the presence of the intense absorption band in the spectra of all nickel hydride complexes (except $Ni_{15}H_{20}^+$), it is most likely that part of the hydrogen is molecularly bound in these complexes. The absence of bands due to D−D stretch vibrations implies that part of the electrons in the nickel hydride complexes with more than 10 nickel atoms are delocalized. It has indeed been shown that the cluster charge is delocalized over the surface of the cluster.[57,58] However, a combination of a theoretical and more detailed spectroscopic study is needed to identify the reason for the absence of a D−D stretch absorption band for the nickel hydride complexes with more than 10 nickel atoms.

6. Comparison. A compilation of the vibrational frequencies for similarly bound hydrogen species bound to the different metals investigated in this study is given in Table 1.

The stretch vibration of hydrogen atoms bridge (μ_2) bound to vanadium, iron, and cobalt clusters does not strongly depend on the metal. However, the vibrational frequency of bridge (μ_2) bound hydrogen to scandium is significantly lower than that of hydrogen bridge (μ_2) bound to vanadium, iron or cobalt. This indicates that the Sc_nO^+−H bond is significantly different than the V_n^+−H, Fe_n^+−H, and Co_n^+−H bonds. Also the vibrational frequencies of face (μ_3) bound hydrogen to vanadium, cobalt, and nickel clusters are rather similar, suggesting that the bond strengths are rather similar. Indeed, the V_n^+−D, Fe_n^+−D, Co_n^+−D, and Ni_n^+−D bond dissociation energies are remarkably similar.[4,6−8] Unfortunately, no quantitative information is available on Sc_nO^+−D bond dissociation energies.

V. Conclusions

The vibrational spectra of a series of transition metal hydride complexes reported here represent a direct probe of atomic and molecular hydrogen binding to cationic metal clusters. Several element and size dependent absorption features are identified. Nickel clusters show distinctly different behavior compared to the other transition metals that were studied. Nickel clusters bind much more hydrogen and a significant part of the adsorbed hydrogen is molecularly chemisorbed. Density functional theory calculations on hydrogen saturated $Sc_nH_mO^+$, $V_nH_m^+$, $Fe_nH_m^+$, $Co_nH_m^+$, and $Ni_nH_m^+$ complexes containing 4, 5, and 6 metal atoms generally provide good agreement with experimental measurements. In contrast to what is observed for extended metal surfaces, where hydrogen has a preference for high coordination sites, hydrogen bound to transition metal clusters of scandium, vanadium, iron, and cobalt can be bound in both bridge and face sites. For nickel no indications for bridge bound hydrogen were found. All hydrogen atoms are bound to the surface of the metal cluster, structures with hydrogen located inside the metal cluster are found to be much higher in energy. A clear transition from molecular to bulk like behavior has not been observed.

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Supporting Information Available: Fabrication process of the ^{58}Ni rod, tables of vibrational spectral data, tables of atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Knickelbein, M. B. *Annu. Rev. Phys. Chem.* **1999**, *50*, 79.
(2) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **2001**, *52*, 423.
(3) Zakin, M. R.; Cox, D. M.; Whetten, R. L.; Trevor, D. J.; Kaldor, A. *Chem. Phys. Lett.* **1987**, *135*, 223.
(4) Liyanage, R.; Conceição, J.; Armentrout, P. B. *J. Chem. Phys.* **2002**, *116*, 936.
(5) Conceição, J.; Liyanage, R.; Armentrout, P. B. *Chem. Phys.* **2000**, *262*, 115.
(6) Conceição, J.; Loh, S. K.; Lian, L.; Armentrout, P. B. *J. Chem. Phys.* **1996**, *104*, 3976.
(7) Liu, F.; Armentrout, P. B. *J. Chem. Phys.* **2005**, *122*, 194320.
(8) Liu, F.; Liyanage, R.; Armentrout, P. B. *J. Chem. Phys.* **2002**, *117*, 132.
(9) Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590.
(10) Conceição, J.; Laaksonen, R. T.; Wang, L.-S.; Guo, T.; Nordlander, P.; Smalley, R. E. *Phys. Rev. B* **1995**, *51*, 4668.
(11) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *Phys. Rev. Lett.* **1985**, *54*, 1494.
(12) Bérces, A.; Berces, A.; Hackett, P. A.; Lian, L.; Mitchell, S. A.; Rayner, D. M. *J. Chem. Phys.* **1998**, *108*, 5476.
(13) Swart, I.; Fielicke, A.; Redlich, B.; Meijer, G.; Weckhuysen, B. M.; de Groot, F. M. F. *J. Am. Chem. Soc.* **2007**, *129*, 2516.
(14) Morse, M. D.; Geusic, M. E.; Heath, J. R.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 2293.
(15) Parks, E. K.; Liu, K.; Richtsmeier, S. C.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *82*, 5470.
(16) Yang, S.; Knickelbein, M. B. *Z. Phys. D Atom Mol. Cl.* **1994**, *31*, 203.
(17) Knickelbein, M. B. *Phys. Rev. B* **2005**, *71*, 184442.
(18) Yuan, H. K.; Chen, H.; Ahmed, A. S.; Zhang, J. F. *Phys. Rev. B* **2006**, *74*, 144434.
(19) Dietrich, G.; Dasgupta, K.; Lützenkirchen, K.; Schweikhard, L.; Ziegler, J. *Chem. Phys. Lett.* **1996**, *252*, 141.
(20) Dietrich, G.; Dasgupta, K.; Kuznetsov, S.; Lutzenkirchen, K.; Schweikhard, L.; Ziegler, J. *Int. J. Mass Spectrom.* **1996**, *157−158*, 319.
(21) Hamrick, Y. M.; Morse, M. D. *J. Phys. Chem.* **1989**, *93*, 6494.
(22) Holmgren, L.; Rosén, A. *J. Chem. Phys.* **1999**, *110*, 2629.
(23) Zakin, M. R.; Cox, D. M.; Brickman, R.; Kaldor, A. *J. Phys. Chem.* **1989**, *93*, 6823.
(24) Richtsmeier, S. C.; Parks, E. K.; Liu, K.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *82*, 3659.
(25) Knickelbein, M. B. *Chem. Phys. Lett.* **2002**, *353*, 221.
(26) Knickelbein, M. B.; Koretsky, G. M.; Jackson, K. A.; Pederson, M. R.; Hajnal, Z. *J. Chem. Phys.* **1998**, *109*, 10692.
(27) Korsgen, H.; Murtz, P.; Lipus, K.; Urban, W.; Towle, J. P.; Brown, J. M. *J. Chem. Phys.* **1996**, *104*, 4859.
(28) Ho, J.; Zhu, L.; Parks, E. K.; Riley, S. J. *Z. Phys. D* **1993**, *26*, 331.
(29) Ho, J.; Zhu, L.; Parks, E. K.; Riley, S. J. *J. Chem. Phys.* **1993**, *99*, 140.
(30) Parks, E. K.; Nieman, G. C.; Riley, S. J. *Surf. Sci.* **1996**, *355*, 127.
(31) Cox, D. M.; Fayet, P.; Brickman, R.; Hahn, M. Y.; Kaldor, A. *Catal. Lett.* **1990**, *4*, 271.
(32) Fielicke, A.; von Helden, G.; Meijer, G.; Pedersen, D. B.; Simard, B.; Rayner, D. M. *J. Phys. Chem. B* **2004**, *108*, 14591.
(33) Fielicke, A.; Kirilyuk, A.; Ratsch, C.; Behler, J.; Scheffler, M.; von Helden, G.; Meijer, G. *Phys. Rev. Lett.* **2004**, *93*, 023401.
(34) Ratsch, C.; Fielicke, A.; Kirilyuk, A.; Behler, J.; von Helden, G.; Meijer, G.; Scheffler, M. *J. Chem. Phys.* **2005**, *122*, 124302.
(35) Oepts, D.; van der Meer, A. F. G.; van Amersfoort, P. W. *Infrared Phys. Technol.* **1995**, *36*, 297.
(36) von Helden, G.; van Heijnsbergen, D.; Meijer, G. *J. Phys Chem. A* **2003**, *107*, 1671.
(37) Oomens, J.; Tielens, A.; Sartakov, B. G.; von Helden, G.; Meijer, G. *Astrophys. J.* **2003**, *591*, 968.
(38) Liu, K.; Parks, E. K.; Richtsmeier, S. C.; Pobo, l. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *83*, 2882.
(39) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
(40) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119.

(41) Eichkorn, K.; Treutler, O.; Oehm, H.; Haeser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283.
(42) Schafer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(43) Knickelbein, M. B. *J. Chem. Phys.* **2002**, *116*, 9703.
(44) Ashman, C.; Khanna, S. N.; Pederson, M. R. *Chem. Phys. Lett.* **2003**, *368*, 257.
(45) Castro, M.; Jamorski, C.; Salahub, D. R. *Chem. Phys. Lett.* **1997**, *271*, 133.
(46) Grigoryan, V. G.; Springborg, M. *Phys. Rev. B* **2004**, *70*, 205415.
(47) Parks, E. K.; Zhu, L.; Ho, J.; Riley, S. J. *J. Chem. Phys.* **1994**, *100*, 7206.
(48) Gruene, P.; Fielicke, A.; Meijer, G. Unpublished results.
(49) Jiang, L.; Xu, Q. *J. Phys Chem. A* **2006**, *110*, 5636.
(50) Jones, N. O.; Beltran, M. R.; Khanna, S. N.; Baruah, T.; Pederson, M. R. *Phys. Rev. B* **2004**, *70*, 165406.
(51) Andersson, S.; Harris, J. *Phys. Rev. Lett.* **1982**, *48*, 545.
(52) Kubas, G. J. *J. Organomet. Chem.* **2001**, *635*, 37.
(53) Udovic, T. J.; Rush, J. J.; Berk, N. F.; Anderson, I. S. *Phys. Rev. B* **1992**, *45*, 12573.
(54) Kohler, C.; Seifert, G.; Frauenheim, T. *Chem. Phys.* **2005**, *309*, 23.
(55) Moritz, W.; Imbihl, R.; Behm, R. J.; Ertl, G.; Matsushima, T. *J. Chem. Phys.* **1985**, *83*, 1959.
(56) Ernst, K. H.; Schwarz, E.; Christmann, K. *J. Chem. Phys.* **1994**, *101*, 5388.
(57) Fielicke, A.; von Helden, G.; Meijer, G.; Pedersen, D. B.; Simard, B.; Rayner, D. M. *J. Chem. Phys.* **2006**, *124*, 194305.
(58) Swart, I.; Fielicke, A.; Rayner, D. M.; Meijer, G.; Weckhuysen, B. M.; de Groot, F. M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5317.