

Molecular adsorption of H₂ on small cationic nickel clusters^{†‡}

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An H₂ molecule can bind molecularly on Ni₄⁺ but it binds exclusively dissociatively on Ni₅⁺ and Ni₆⁺ and the adsorption behavior correlates with the relative reactivity of the metal clusters towards H₂.

The adsorption of H₂ on metal clusters is of interest in several fields, including metallurgy, catalysis and hydrogen storage. Hydrogen interacting with small Ni clusters is of special interest, as Ni is widely used as a hydrogenation catalyst. In general, reactions of H₂ with extended Ni surfaces are well studied, both experimentally¹ and theoretically.² In practically all cases an H₂ molecule dissociates upon adsorption on a Ni surface and the H atoms bind in high coordination sites. The dissociation of H₂ on Ni is direct, *i.e.* it does not proceed *via* a molecular precursor state.^{1,3} H₂ molecules can only bind molecularly on the step sites of a Ni(510) surface if this surface is fully saturated with H atoms.⁴ Small Ni clusters do not necessarily exhibit the same behavior as extended surfaces. Consequently, the reaction of gas-phase Ni clusters with H₂ has been the subject of many studies.^{5–8} However, detailed information on H binding sites on Ni clusters is scarce. In agreement with what is observed for extended Ni surfaces, it has recently been confirmed by IR spectroscopy that H₂ can be molecularly adsorbed on hydrogen saturated Ni clusters.⁹ It is not clear whether H₂ binds molecularly to nickel clusters only once all sites for dissociative adsorption are blocked, or whether already the very first H₂ molecule can bind molecularly.

Here we report on a vibrational spectroscopy study, complemented with density functional theory (DFT) calculations, on the adsorption of a single H₂ molecule on Ni_{*n*}⁺ clusters with *n* = 4–6. It will be shown that the first H₂ molecule can bind molecularly on Ni₄⁺, but that it binds exclusively dissociatively on Ni₅⁺ and Ni₆⁺. Infrared multiple photon dissociation (IR-MPD) spectroscopy has been used to measure the vibrational spectra of Ni_{*n*}H₂⁺ complexes in the Ni–H stretch and deformation range as well as in the hydrogen–hydrogen stretch range. The setup and experimental

procedures have been described in detail elsewhere.^{10,11} Briefly, metal clusters are generated in a laser ablation source. They pass through a reactor channel where reaction with H₂ occurs under thermalized conditions (at ~25 °C). The extent of complex formation is controlled by adjusting the opening time of the H₂ inlet valve on the reactor channel and the back pressure of H₂ behind that valve. A molecular beam is formed after expansion out of the reactor channel. This beam is shaped by a skimmer and an aperture before being overlapped with a counter-propagating beam of IR photons delivered by the free electron laser for infrared experiments (FELIX).¹² When the laser frequency is resonant with an IR-active vibration of a complex, several photons can be absorbed by the complex and it subsequently can undergo fragmentation. The vibrational spectra can be reconstructed by monitoring the changes in the cluster mass distribution as a function of photon frequency. Deuterium was used to probe the high frequency range because the D–D stretch vibration is located in a spectral range that is easier accessible with FELIX. To prevent congestion of the mass spectra, an isotopically enriched ⁵⁸Ni rod was used.

In Fig. 1A, three mass spectra, measured at different H₂ partial pressures in the reactor, are shown. A clear dependence of the reactivity on cluster size is observed. At low hydrogen content Ni₅⁺ and Ni₆⁺ already bind H₂ but no Ni₄H₂⁺ is found. The Ni₄H₂⁺ complex can only be formed by increasing the hydrogen content in the reactor further. At those pressures, Ni₅⁺ and Ni₆⁺ already bind multiple H₂ molecules. The differences in reactivity can be quantified by assuming that the addition of the first H₂ molecule is irreversible and rate determining in the process of adsorption of multiple H₂ molecules.⁷ Since the molecular H₂ is present in excess, the depletion of the bare nickel clusters should then follow pseudo-first-order kinetics. Assuming that the hydrogen partial pressure in the reactor channel is proportional to the backpressure of H₂ in the pulsed valve, a semilogarithmic plot of the fraction of bare Ni clusters remaining at a certain H₂ concentration, *f*, versus the back pressure should give a straight line with a slope proportional to the rate constant. Such plots are shown in Fig. 1B. The good fit of the experimental data to the pseudo-first-order model indicates that the kinetic scheme outlined above is a reasonable approximation. Under the assumption that the reaction time is similar for all

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[†] Electronic supplementary information (ESI) available: Details of the calculations, energies, geometries and vibrational spectra of all calculated isomers. See DOI: 10.1039/b807313a

[‡] This paper is dedicated to David M. Rayner on the occasion of his 60th birthday.

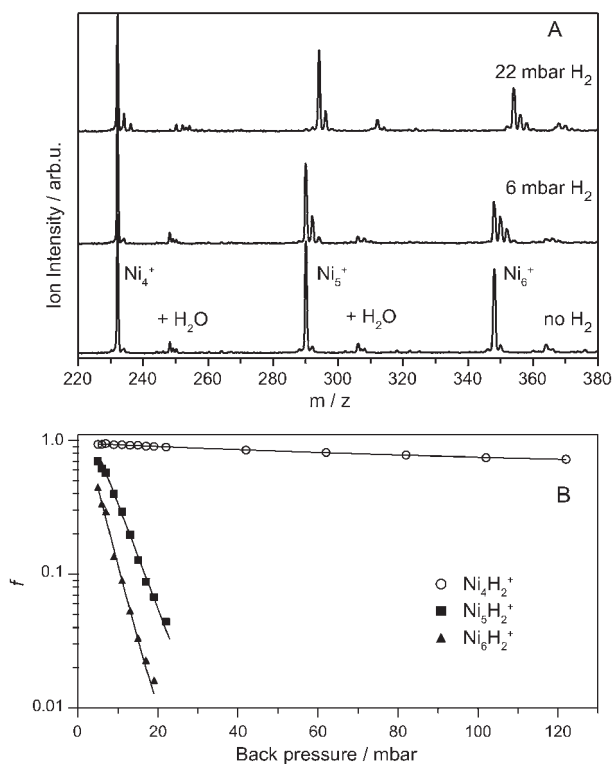


Fig. 1 A. Mass spectra taken at various H₂ concentrations in the reactor, using backpressures ranging from no H₂ (bottom) to 22 mbar (top). Several peaks due to nickel water complexes are present in the spectrum. B. Semilogarithmic plot of the fraction of unreacted Ni clusters, *f*, versus the H₂ back pressure.

cluster sizes, the relative reactivity of Ni₄⁺, Ni₅⁺, and Ni₆⁺ toward H₂ scales as 1 : 65 : 85. This differs significantly from the ratio of the rate constants for the formation of Ni₅D₂⁺ and Ni₆D₂⁺ measured under single collision conditions ($0.15 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively).⁵ These differences can be understood by a rapid stabilization of the complex *via* collisional thermalization in our reaction channel, which is missing under single collision conditions.

Consistent with the high reactivity of Ni₅⁺ and Ni₆⁺, collision induced dissociation experiments have found no significant barriers for the formation of Ni₅D₂⁺ and Ni₆D₂⁺. Ni₄D₂⁺ is not stable after formation under single collision conditions.⁵ Barriers to the formation of M_{*n*}D₂ complexes have been found for cobalt and iron clusters of certain size.¹³ It is possible that such barriers lead to a stabilization of a precursor state to dissociation in which the hydrogen is molecularly coordinated. However, such a state has never been directly observed experimentally.

To probe how hydrogen is bound in Ni₄H₂⁺, Ni₅H₂⁺, and Ni₆H₂⁺, the vibrational spectra of these complexes were recorded under conditions such that only complexes with a single H₂ molecule were present in the molecular beam. Because Ni₄⁺ is much less reactive than Ni₅⁺ and Ni₆⁺, different conditions had to be used to measure the vibrational spectra of these three complexes. The experimental vibrational spectra of Ni_{*n*}H₂⁺/Ni_{*n*}D₂⁺ (*n* = 4–6) complexes are shown in black in Fig. 2. For the complexes with 5 and 6 Ni atoms,

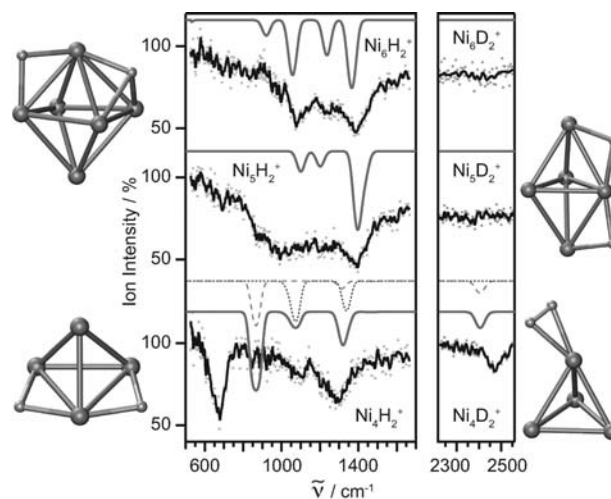


Fig. 2 Experimental (black) and simulated (red) spectra of Ni₄H₂⁺, Ni₅H₂⁺ and Ni₆H₂⁺ (bottom to top). The corresponding geometries are shown next to the spectra. The simulated spectrum of Ni₄H₂⁺ is a linear combination with a ratio of 4 : 1 of the spectra of the isomer with molecular H (green dashed line) and dissociated H (blue dotted line) respectively. The experimental spectra are overlaid with a three-point running average to guide the eye.

intense absorption bands are observed in the 1000–1500 cm⁻¹ range, implying that the H is predominantly dissociatively bound in bridging or face sites.⁹ For the Ni₄D₂⁺ complex, a band located at 2460 cm⁻¹ is observed, proving that there is at least one isomer present in which the D₂ molecule is molecularly bound. The frequency of the D–D stretch band is shifted considerably to lower frequency compared to the frequency of free D₂ (2941 cm⁻¹). This implies that the molecularly bound D₂ molecules must be chemisorbed since physisorbed species only show small frequency shifts.¹⁴ A strong absorption band at 680 cm⁻¹ is observed in the spectrum of Ni₄H₂⁺ but not in the spectra of Ni₅H₂⁺ and Ni₆H₂⁺, which again points to a different binding of the hydrogen in Ni₄H₂⁺ compared to Ni₅H₂⁺ and Ni₆H₂⁺. Such bands have been assigned to the Ni–(H₂) stretch vibration, $\nu(\text{Ni}-(\text{H}_2))$.⁹ Comparison of the IR-MPD spectrum with simulated spectra supports this assignment. The molecular adsorption of H₂ on Ni₄⁺ is remarkable as sites for dissociatively bound H atoms are available and as the dissociative chemisorption of H₂ on nickel surfaces does not proceed *via* a molecular precursor state.

To obtain information on adsorption geometries and bond energies, DFT calculations were performed. The spin and symmetry unrestricted calculations employed the BP86 exchange correlation functional and a TZVPP basis set. Vibrational frequencies and IR intensities were calculated within the harmonic approximation. It has been shown that this approach gives good agreement with experiment.^{9,10} Initial complex geometries were generated based on bare metal structures proposed in the literature. For each geometric isomer, calculations were performed for several different spin states. It is known that adsorption of H₂ decreases the total magnetic moment of Ni clusters.⁸ Species with molecular or dissociatively bound H are found to be (local) energetic minima. Upon substitution of H by D, all modes, except the

Ni–Ni modes, scale down in frequency by a factor close to $\sqrt{2}$ ($\pm 1.2\%$). The energy differences between isomers are very small, typically $\Delta E < 0.2$ eV, which is within the expected accuracy of the calculations. Hence, a ground state geometry cannot be assigned based on energetic considerations alone. Simulated vibrational spectra that provide reasonable agreement with the experimental spectra are shown in Fig. 2 (red) together with the corresponding optimized cluster geometries. Note that the actual structures can be different from the ones shown in Fig. 2. For Ni_4H_2^+ , two isomers are required to account for all the absorption features observed in the experimental spectrum (see below). Relative energies, geometries, and vibrational spectra of other isomers can be found in the supplementary information.[†] In agreement with experiment, the hydrogen atoms are dissociatively bound in the isomers of Ni_5H_2^+ and Ni_6H_2^+ whose vibrational spectra are in best agreement with the experimental spectra. Complexes with molecularly bound H_2 are at least 0.4 eV higher in energy. In contrast, for Ni_4H_2^+ , the lowest energy isomer identified in the calculations, is the complex with molecularly bound H_2 . The binding energy of the H_2 molecule is calculated to be 0.5 eV. The calculated frequency of $\nu(\text{D}-\text{D})$ is too low compared to experiment, while the calculated frequency of $\nu(\text{Ni}-(\text{H}_2))$ is too high. Both of these observations imply that the calculations overestimate the Ni– H_2 bond strength.⁹ In the experimental spectrum of Ni_4H_2^+ there is a weak absorption band at ~ 1090 cm^{-1} , for which the complex with molecular hydrogen cannot account. It is possible that this band is due to the presence of a second, less abundant isomer in which the hydrogen is dissociatively bound. Indeed the calculations show that there are at least two isomers that have an absorption band around 1090 cm^{-1} and which are nearly iso-energetic ($\Delta E = 0.1$ eV), with the complex containing molecularly bound H_2 . Hence, it is likely that two isomers of Ni_4H_2^+ , one with molecularly bound and one with dissociatively bound hydrogen, coexist in the molecular beam. The structures of the complex with molecularly bound hydrogen and of a nearly iso-energetic isomer with dissociatively bound hydrogen are shown in Fig. 2, together with a simulated vibrational spectrum that is a linear combination with a 4 : 1 ratio (isomer with molecular H versus isomer with dissociated H) of the spectra of the two individual isomers.

In conclusion, we have demonstrated that a H_2 molecule can bind molecularly on Ni_4^+ but that it binds exclusively dissociatively on Ni_5^+ and Ni_6^+ . Furthermore, the adsorption behavior correlates with the relative reactivity of the metal

clusters toward H_2 . This correlation implies that the dissociative chemisorption of H_2 on Ni_4^+ is an indirect process; for other small nickel clusters low barriers might exist as well. In that case, the rate determining step is the conversion of the molecular precursor state to the final state where the hydrogen is dissociatively bound. The Ni_4H_2^+ isomer with molecular bound H_2 could be considered as a model for a precursor state to dissociation.

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