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The effect of D_2/H_2 substitution on the $Nb_n^+ + H_2$ reaction

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Abstract. The effect of D_2/H_2 substitution on the reactions of niobium cluster cations Nb_n^+ ($n = 5 - 9$) with hydrogen was studied using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer combined with a laser-ablation/supersonic-jet external ion source. For most cluster sizes, it has been found that the reactions of the Nb_n^+ clusters with H_2/D_2 mixture yield considerable amounts of Nb_nHD^+ even at small conversion of Nb_n^+. These results suggest a mechanism which involves the dissociative chemisorption of H_2 on the niobium cluster, followed by the competing stabilization and back dissociation of the energized adduct.

PACS. 36.40.Jn Reactivity of clusters – 36.40.Wa Charged clusters – 82.80.Ms Mass spectrometry

1 Introduction

Despite numerous studies of the adsorption of hydrogen on niobium cluster cations [1–7], the mechanism of this reaction is still far from being fully understood. All authors have reported that H_2 reacts with Nb_n^+ clusters *via* sequential attachment of hydrogen molecules. Zakin *et al.* [4] and Elkind *et al.* [5] have claimed that this process is the dissociative chemisorption. Berg *et al.* [6] have pointed out the importance of the physisorption stage in the reactions of the Nb_n^+ clusters with hydrocarbons, and have suggested that in the $Nb_n^+ + H_2$ reaction, the formation of the long-lived physisorbed complex may be an alternative to the dissociative chemisorption.

In our previous paper [7], we reported the relative rate constants for the sequential attachment of hydrogen to niobium cluster cations. We found that the reactivity of the clusters towards hydrogen strongly depends on the amount of adsorbed H_2 molecules. In some cases (e.g., Nb_8^+ and Nb_{11}^+), the reactivity increases after the adsorption of a hydrogen molecule. This suggests that the attachment of hydrogen changes the electronic structure of the cluster; therefore, the process involved is chemisorption rather than physisorption.

In the present investigation, we used an H_2/D_2 mixture instead of pure H_2 in order to clarify the mechanism of the reactions of Nb_n^+ clusters with hydrogen in further detail. The obtained data support the dissociative chemisorption mechanism.

2 Experimental

The general description of the experimental setup with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Finnigan, FTMS-2000, magnetic field 3 T, dual cell) was presented earlier [7]. However, some experimental procedures have been changed. Instead of leak valves, pulsed gas valves are used for the admission of both reactant and buffer gas. This allows a higher flexibility in designing experiments with the FT-ICR. In principle, it is possible to construct an arbitrary sequence of trapping, thermalization, rf or SWIFT [8, 9] excitation (or ejection), detection of selected ions, and controlled admission of inert and reactant gases. These processes are separated in time and occur in the same compartment of the dual ion cyclotron resonance (ICR) cell.

The details of the new arrangement of the setup and experimental procedures will be presented elsewhere [10]. Niobium cluster cations were produced by the use of a compact laser-ablation/supersonic-jet external ion source [7] similar to that described by Maruyama *et al.* [11]. The Nb_n^+ cluster cations ($n = 2 - 12$) were produced without any additional ionization source. The cluster cations trapped in the ICR cell were thermalized by a pulse of argon produced by a solenoid pulsed valve (General Valve, opening time 350 μs, backing pressure 1 atm). The amount of argon introduced into the ICR cell per pulse was chosen so that each cluster underwent at least 1×10^3 collisions with argon atoms; this was considered to be sufficient for the translational thermalization of the clusters. After the complete pumping of the buffer

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gas out of the ICR cell, the H_2/D_2 mixture with a molar ratio of $H_2 : D_2 = 1 : 0.95$ was admitted as a series of pulses at a repetition rate of 10 Hz (General Valve, opening time 130–200 μs, backing pressure 1 atm). The excitation/detection cycle was performed only after the complete pumping of H_2 out of the cell, *i.e.*, in a few seconds. The course of the reaction was monitored as the relative abundance of the reactants and reaction products *versus* the number of applied hydrogen pulses.

3 Results and discussion

In the studies of the $Nb_n^+ + H_2$ reactions reported so far [4–7], the only products observed have been the hydrides $Nb_nH_2^+$, $Nb_nH_4^+$, $Nb_nH_6^+$, etc., which are apparently formed by the sequential attachment of hydrogen to niobium cluster cations. The primary goal of this study was the synthesis and collision-induced dissociation (CID) of partially deuterated niobium cluster hydrides (e.g., $Nb_nH_2D_2^+$). We sought to determine if the dissociation of these D-substituted hydrides could yield HD, because the elimination of HD would support the dissociative chemisorption mechanism of the $Nb_n^+ + H_2$ reactions.

To synthesize the mixed hydrides, we used the H_2/D_2 mixture instead of pure H_2 as a reactant. Although the Nb_n^+ clusters with $n = 2-12$ could be produced, the data on the reactions with H_2/D_2 are reported only for $n = 5-9$. For Nb_4^+, Nb_{10}^+, and Nb_{11}^+, we could not perform reliable measurements. The reactivities of these clusters towards hydrogen are relatively low [5–7], whereas their reactivities towards O_2 [12,13] or H_2O [6] are high. Therefore, even trace amounts of O_2 and/or H_2O in the H_2/D_2 sample gave rise to high yields of niobium cluster oxides, which interfered with the measurements. The Nb_2^+, Nb_3^+, and Nb_{12}^+ clusters are inert towards hydrogen molecules under the present experimental conditions [5–7].

We expected the sequential attachment of H_2 and D_2 to Nb_n^+ to yield $Nb_nH_2^+$ and $Nb_nD_2^+$ in the first stage, $Nb_nH_4^+$, $Nb_nD_4^+$, and $Nb_nH_2D_2^+$ in the second stage, and higher hydrides containing even numbers of H and D atoms in subsequent stages. However, for most niobium cluster cations, the formation of the Nb_nHD^+ adducts was observed even in the initial stage of the reaction, at small conversion of Nb_n^+. Figures 1–3 show three representative examples: (i) Nb_7^+, which gives the largest extent of H/D scrambling; (ii) Nb_8^+, where almost no Nb_8HD^+ is observed, and (iii) Nb_9^+, which is an intermediate case with a low yield of Nb_9HD^+. For Nb_5^+ and Nb_6^+, the results were similar to the case of Nb_7^+, i.e., the yield of Nb_nHD^+ was rather high. It is also clearly seen from Figs. 1 and 3 that the kinetic curves of the accumulation of Nb_nHD^+ are S-shaped, which is indicative of the delayed formation of the product.

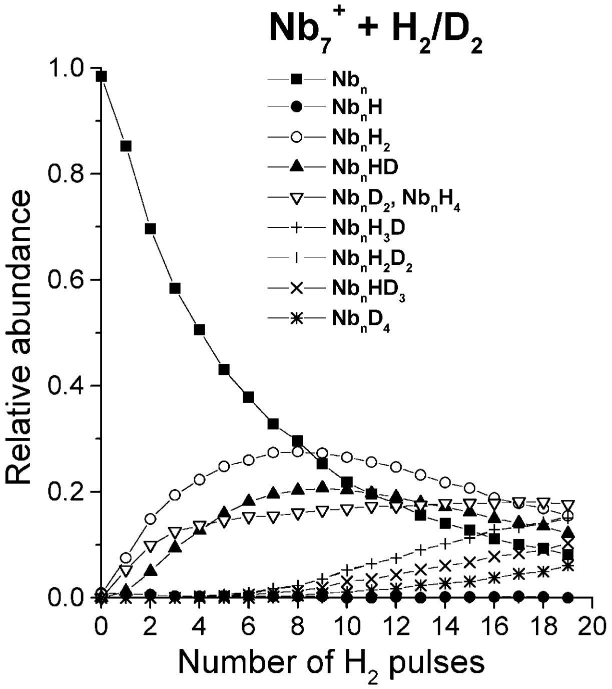

Fig. 1. The kinetic curves for the $Nb_7^+ + H_2/D_2$ reaction. The yield of Nb_7HD^+ is comparable to that of $Nb_7H_2^+$ and $Nb_7D_2^+$. The kinetic curve of the Nb_7HD^+ accumulation is S-shaped. Pulsed-valve opening time was 140 μs.

The following simplified scheme of the $Nb_n^+ + H_2$ reaction is consistent with the experimental observations:

$$\begin{tikzcd}
Nb_n^+ \arrow[r, shift left, "+H_2(k_r)"] & {[Nb_nH_2^+]^*} \arrow[l, shift left, "-H_2(k_d)"] \arrow[r, shift left, "+H_2(k'_r)"] \arrow[d, "(k_s)"] & {[Nb_nH_4^+]^*} \arrow[l, shift left, "-H_2(k'_d)"] \arrow[r, shift left, "+H_2(k''_r)"] \arrow[d, "(k'_s)"] & {[Nb_nH_6^+]^* \ldots} \arrow[l, shift left, "-H_2(k''_d)"] \arrow[d, "(k''_s)"] \\
 & Nb_nH_2^+ & Nb_nH_4^+ & Nb_nH_6^+
\end{tikzcd}$$

In this mechanism, the attachment of each H_2 molecule involves the association (k_r) followed by the competing collisional (and/or radiative) stabilization (k_s) and back dissociation (k_d) of the energized adduct $[Nb_nH_{2m}^+]^*$. By the term "stabilization" we mean the stabilization with respect to the back dissociation only, which may not substantially affect the reactivity of the adduct towards the next hydrogen molecule. The association stages involve the H−H bond rapture accompanied by the formation of two Nb−H chemical bonds, *i.e.*, it is the dissociative chemisorption rather than physisorption (the dissociative chemisorption of H_2 toward Nb_n^+ may be slightly exothermic since the H−H binding energy is 432 kJ mol^{-1}, while the binding energy for $Nb^+{-}H$ is 222 kJ mol^{-1} [14]). The sequence of the reversible dissociative chemisorption stages is responsible for the H/D scrambling in the reaction products. The mechanism is also consistent with the observed S-shaped kinetic curves of the Nb_nHD^+ accumulation.

Another observation that supports the above mechanism is the correlation between the observed yields of

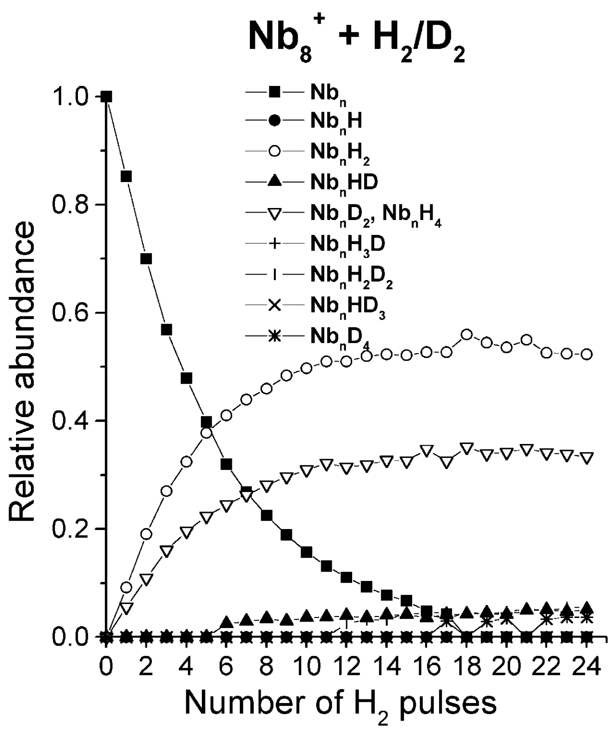

Fig. 2. The kinetic curves for the $Nb_8^+ + H_2/D_2$ reaction. Almost no Nb_8HD^+ forms. Pulsed-valve opening time was 150 μs.

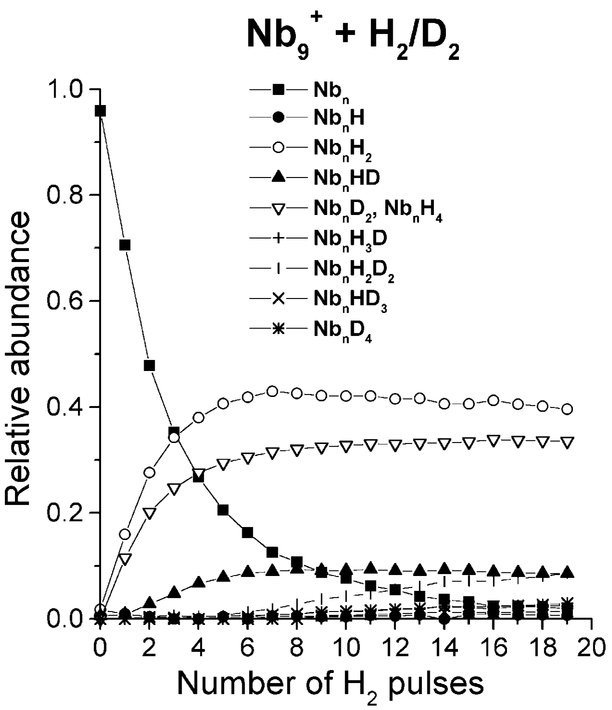

Fig. 3. The kinetic curves for the $Nb_9^+ + H_2/D_2$ reaction. The yield of Nb_9HD^+ is intermediate between the cases of Nb_7^+ and Nb_8^+. The kinetic curve of the Nb_9HD^+ accumulation is S-shaped. The pulsed-valve opening time was 140 μs.

Nb_nHD^+ in the first stage of the $Nb_n^+ + H_2/D_2$ reaction and the rate constants of the attachment of the second and the third H_2 molecules to the cluster. For Nb_n^+ with $n = 5, 6$, and 7, the rate constants of the attachment of the second and third hydrogen molecules (k_2 and k_3, respectively) are almost the same as the rate constant of the attachment of the first H_2 molecule (k_1), *i.e.*, $k_1 \approx k_2 \approx k_3$ [7]. For Nb_8^+, $k_1 \approx k_3 \gg k_2$, while for Nb_9^+, $k_1 \gg k_2 \gg k_3$ [7]. According to the above scheme, the lower k_2 should lead to the lower yield of Nb_nHD^+. Hence, for Nb_8^+ and Nb_9^+, one may expect the Nb_nHD^+ yields to be lower than those for Nb_5^+, Nb_6^+, and Nb_7^+. In the case of Nb_8^+, where the least extent of H/D scrambling is observed, the back dissociation of the $[Nb_8H_2D_2^+]^*$ adduct *via* HD elimination (which is the main channel of Nb_8HD^+ formation) is likely to be suppressed by the fast reaction of the adduct with the third hydrogen molecule. This is probably the reason for the extremely low yield of Nb_8HD^+. For Nb_9^+, the attachment of the third hydrogen molecule is slow; therefore, the yield of Nb_9HD^+ is higher than in the case of Nb_8^+.

Preliminary experiments on the collision-induced dissociation (CID) of $Nb_7H_3D^+$ and $Nb_7H_2D_2^+$ clusters in the ICR cell (with argon as a target gas) have shown that $Nb_7H_3D^+$ dissociates to yield $Nb_7H_2^+$ and Nb_7HD^+, the product branching ratio being close to 1 : 1. The CID of $Nb_7H_2D_2^+$ gives $Nb_7H_2^+$, Nb_7HD^+, and $Nb_7D_2^+$, at relative yields of about 1 : 4 : 1. These results give direct evidence that the adsorption of hydrogen molecules on Nb_n^+ clusters is dissociative chemisorption.

4 Conclusions

It has been found that for most Nb_n^+ clusters ($n = 5 - 9$), the $Nb_n^+ + H_2/D_2$ reaction yields a considerable amount of Nb_nHD^+, even at small conversion of Nb_n^+. The relative yields of Nb_nHD^+ correlate with the rate constants of the attachment of the second and third H_2 molecules to the cluster. The experimental observations can be explained by the consideration of a reaction scheme where the attachment of each hydrogen molecule to the cluster involves the association stage followed by the competing collisional (and/or radiative) stabilization and back dissociation of the energized adduct $[Nb_nH_{2m}^+]^*$. The production of Nb_nHD^+ in the $Nb_n^+ + H_2/D_2$ reaction suggests that the association stage probably involves the H−H bond rapture accompanied by the formation of two Nb−H chemical bonds, *i.e.*, it is dissociative chemisorption. Preliminary experiments on the collision-induced dissociation of $Nb_7H_3D^+$ and $Nb_7H_2D_2^+$ clusters support this conclusion.

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