Reaction of carbon monoxide and hydrogen on neutral Nb₈ clusters in the gas phase
Y. Xie and S.-G. He F. Dong and E. R. Bernstein

Citation: The Journal of Chemical Physics 128, 044306 (2008); doi: 10.1063/1.2813348
View online: http://dx.doi.org/10.1063/1.2813348
View Table of Contents: http://aip.scitation.org/toc/jcp/128/4
Published by the American Institute of Physics
Reaction of carbon monoxide and hydrogen on neutral Nb$_8$ clusters in the gas phase

Y. Xie and S.-G. He  
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA

F. Dong and E. R. Bernstein  
Department of Chemistry and NSF ERC for Extreme Ultraviolet Science and Technology, Colorado State University, Fort Collins, Colorado 80523-1872, USA

(Received 28 November 2006; accepted 24 October 2007; published online 25 January 2008)

Reactions of neutral V$_n$, Nb$_n$, and Ta$_n$ metal clusters ($n \leq 11$) with CO+H$_2$ mixed gases and CH$_3$OH in a flow tube reactor ($1–50$ Torr) are studied by time of flight mass spectroscopy and density functional theory calculations. Metal clusters are generated by laser ablation, and reactants and products are ionized by low fluence ($\sim 200$ $\mu$J/cm$^2$) 193 nm excimer laser light. Nb$_8$ clusters exhibit strong size dependent reactivity in reactions both with CO+H$_2$ and CH$_3$OH compared with V$_n$ and Ta$_n$ clusters. A “magic number” (relatively intense) mass peak at Nb$_8$COH$_4$ is observed in the reaction of Nb$_8$ clusters with CO+H$_2$, and CH$_3$OH is suggested to be formed. This feature at Nb$_8$COH$_4$ remains the most intense peak independent of the relative concentrations of CO and H$_2$ in the flow tube reactor. No other Nb$_n$, Ta$_n$, or V$_n$ feature behaves in this manner. In reactions of CH$_3$OH with metal clusters M$_n$ ($M=V$, Nb, and Ta, $n=3–11$), nondehydrogenated products M$_n$COH$_4$/M$_n$CH$_3$OH are only observed on Nb$_8$ and Nb$_{10}$, whereas dehydrogenated products M$_n$CO/CM$_x$O are observed for all other clusters. These observations support the suggestion that CH$_3$OH can be formed on Nb$_8$ in the reaction of Nb$_n$ with CO+H$_2$. A reaction mechanism is suggested based on the experimental results and theoretical calculations of this work and of those in the literature. Methanol formation from CO+H$_2$ on Nb$_8$ is overall barrierless and thermodynamically and kinetically favorable. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2813348]

I. INTRODUCTION

Methanol synthesis from carbon monoxide and hydrogen,

$$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad (\Delta H_{298} = -91 \text{ kJ/mol}), \quad (1)$$

is an important industrial process, and it offers a clear economic and political advantage compared with oil refining. Methanol is not only an essentially fundamental feedstock for the chemical industry but it is also a clean liquid fuel and can be utilized in automobiles and other (e.g., fuel cell) applications. The syngas (CO+H$_2$) catalytic reaction to produce CH$_3$OH has attracted deep interest for nearly a century. Most catalysis studies are focused on condensed phase reactions, but a few studies are done with gas phase systems. Clusters are good models to simulate active sites of complex solid state catalysts. Molecular level mechanisms for condensed phase catalytic reactions may be understood through the study of gas phase model reactions. Moreover, theoretical calculations can be used to help us in the interpretation of experimental results and the prediction of detailed reaction mechanisms for finite cluster systems.

A number of studies have been carried out for the reaction of M$_n$ ($M=V$ and Nb) with CO and H$_2$, and a brief review for these systems is given below. Neutral transition metal clusters (M$_n$) are typically generated by laser ablation of the metal and two different apparatuses are employed to investigate their reactivity. One is called a fast flow or flow tube reactor, and the other is called a pickup cell. The major difference between the two cells is that seeded reactant gas ($A, B, etc.$) in a large amount of inert buffer gas ($\sim 1–50$ Torr) is used in the flow tube reactor, while low pressure ($\sim 1$ mTorr) pure reactant gas is used in the pickup cell. As a result, collision intermediates (M$_n$A) can be stabilized by the buffer gas in the flow tube reactor and reactant species can be additionally cooled. There is no buffer gas to stabilize the intermediates in the pickup cell so M$_n$A either directly dissociates (M$_n$+A), undergoes further reactive dissociation (C+D, C and D $\neq$ A), or is detected in a metastable state. Consequently, the chemistry in a pickup cell occurs at a much higher temperature ($T \sim 700$ K) than that in a flow tube reactor ($T \sim 300$ K).

Reactions of neutral Nb$_n$ clusters with CO and D$_2$ in a flow tube reactor have been reported by Morse et al., Kal-dor and co-workers, and Bérces et al. The reactivity of Nb$_n$ with CO smoothly increases for $n \geq 3$ with no adsorbed products detected for $n=1$ and 2. The reaction with D$_2$ is observed as a function of cluster size. Nb$_8$, Nb$_{10}$, and Nb$_{16}$ are far less reactive than their neighbor Nb$_n$ clusters in the reaction with D$_2$. Holmgren et al. have studied the reaction of Nb$_n$ with CO in a pickup cell experiment. The first CO adsorption probability exhibits a strong size dependence and

---

4Electronic mail: erb@lamar.colostate.edu.
Nb₈ shows very low reactivity with CO. Their results are different from those for a flow tube experiment in which no drop in reactivity of Nb₈ is observed. Reactions of Vₙ with CO and D₂ (separately) have also been studied in both flow tube22 and pickup19 cell experiments. Strong size dependent reactivity is observed with D₂ but not with CO. No reports are found for the reaction of Taₙ with CO and D₂/H₂, and only reactions with nitrogen, benzene, and aliphatic hydrocarbons are investigated for Taₙ.20,26–28

Previous flow tube reactor studies21–23 suggest that H₂ is dissociatively absorbed on Mₙ (M=V, Nb, . . .), while CO is initially molecularly absorbed on Mₙ clusters. Following initial molecular adsorption, CO can be dissociatively adsorbed on a metal cluster in an activated reaction by surmounting a reaction barrier. This chemistry is probably associated with weak bonding between metal and hydrogen.21

Reactions of Mₙ (M=V and Nb) with CO and H₂ separately are widely investigated in the literature, but the reaction of metal clusters with mixed CO+H₂ has not been previously studied. In this report, we discuss, in particular, the high CO bond strength reaction barrier. This chemistry is probably associated with strong size dependent molecular adsorption, CO can be dissociatively adsorbed on a metal cluster in an activated reaction by surmounting a reaction barrier. This chemistry is probably associated with weak bonding between metal and hydrogen.21

A short summary of our flow tube experimental equipment is given below.

The vacuum system includes two vacuum chambers: the reaction chamber, which is for cluster generation and reaction, and the mass chamber, which is for detection of reactants and products. The two chambers are separated by a skimmer. The motivation for this two chamber design is to maintain a low pressure (10⁻⁶–10⁻⁷ Torr) in the mass chamber. Mₙ clusters are generated by laser ablation with a focused 532 nm laser (Nd³⁺:yttrium aluminum garnet, 10 Hz, 5–8 mJ/pulse, and 8 ns duration) onto a 12 mm diameter spring loaded metal disk [M=V (99.7%), Nb (99.8%), and Ta (99.99%), Sigma-Aldrich] in the presence of high purity (99.995%, Spectra Gas) pulsed helium carrier gas controlled by a R. M. Jordan supersonic nozzle. A translational and rotational (spiral) motion of the disk is managed by a single motor (Maxon) that is powered by a homemade controller with a wide range of speed adjustment. Metal clusters are formed in an adjustable length gas channel with a “waiting room” upstream.15 Typical dimensions used in this system are 3 mm diameter by 5 mm length for the waiting room and 1.8 mm diameter by 44 mm length for the rest of the channel. The gas channel is coupled directly to a tube/reactor (stainless steel, 6.3 mm inner diameter by 76 mm length). The reactant gases, CO and H₂ (99.9% without further purification, General Air), and CH₃OH (99.9%, Sigma-Aldrich) are mixed with helium and injected into the reactor by a second pulsed valve (General Valve, series 9) with a pulse duration of about 1 ms. The delay time between the two valve openings is optimized to yield best product signals. Pressure in the flow tube reactor is estimated to be about 14 Torr in the presence of a reactant gas pulse. After reaction of Mₙ with CO+H₂ or CH₃OH in the reactor, reactants, products, and the buffer gases are expanded into the first chamber (~10⁻³–10⁻⁴ Torr) to form a molecular beam. The beam enters the vacuum of the second, detection mass spectrometer chamber (~10⁻⁶–10⁻⁷ Torr) through a 5 mm diameter skimmer. The clusters and products in the beam are ionized by a 193 nm excimer laser (10 mm by 2 mm rectangle, ~200 μJ/cm²). Ions are accelerated and detected by a time of flight mass spectrometer, and signals are recorded and averaged typically for 2500 laser shots by a digital storage oscilloscope (Tektronix TDS5032B).

B. Calculational

Neutral, cationic, and anionic niobium clusters have been investigated by DFT calculations of their structures,30–33 binding energies,30 and reaction pathways.34,35 In this study, calculations include geometry optimizations, vibrational frequency determination for the neutral Nbₙ cluster, related Nbₙ/CO/H₂ adsorption clusters, and the transition states of the reaction pathway. These DFT calculations are performed employing Becke’s exchange36 and Perdew-Wang correlation37 functional, denoted as BPW91, within the GAUSSIAN 03 package.38 The LANL2DZ basis set, which involves the Los Alamos effective core potential plus a double zeta basis set, is employed to model the niobium atom, and the standard 6-311+G(2d, p) basis set has been used to model carbon, oxygen, and hydrogen atoms. All calculations are carried out with the GAUSSIAN 03 program.38

II. PROCEDURES

A. Experimental

These experiments are carried out in both a flow tube reactor and a pickup cell. The pickup cell setup has been described previously,20 and the design of our flow tube reactor is similar to the one adopted by Geusic et al.11 A short summary of our flow tube experimental equipment is given below.

The vacuum system includes two vacuum chambers: the reaction chamber, which is for cluster generation and reaction, and the mass chamber, which is for detection of reactants and products. The two chambers are separated by a skimmer. The motivation for this two chamber design is to maintain a low pressure (10⁻⁶–10⁻⁷ Torr) in the mass chamber. Mₙ clusters are generated by laser ablation with a focused 532 nm laser (Nd³⁺:yttrium aluminum garnet, 10 Hz, 5–8 mJ/pulse, and 8 ns duration) onto a 12 mm diameter spring loaded metal disk [M=V (99.7%), Nb (99.8%), and Ta (99.99%), Sigma-Aldrich] in the presence of high purity (99.995%, Spectra Gas) pulsed helium carrier gas controlled by a R. M. Jordan supersonic nozzle. A translational and rotational (spiral) motion of the disk is managed by a single motor (Maxon) that is powered by a homemade controller with a wide range of speed adjustment. Metal clusters are formed in an adjustable length gas channel with a “waiting room” upstream.15 Typical dimensions used in this system are 3 mm diameter by 5 mm length for the waiting room and 1.8 mm diameter by 44 mm length for the rest of the channel. The gas channel is coupled directly to a tube/reactor (stainless steel, 6.3 mm inner diameter by 76 mm length). The reactant gases, CO and H₂ (99.9% without further purification, General Air), and CH₃OH (99.9%, Sigma-Aldrich) are mixed with helium and injected into the reactor by a second pulsed valve (General Valve, series 9) with a pulse duration of about 1 ms. The delay time between the two valve openings is optimized to yield best product signals. Pressure in the flow tube reactor is estimated to be about 14 Torr in the presence of a reactant gas pulse. After reaction of Mₙ with CO+H₂ or CH₃OH in the reactor, reactants, products, and the buffer gases are expanded into the first chamber (~10⁻³–10⁻⁴ Torr) to form a molecular beam. The beam enters the vacuum of the second, detection mass spectrometer chamber (~10⁻⁶–10⁻⁷ Torr) through a 5 mm diameter skimmer. The clusters and products in the beam are ionized by a 193 nm excimer laser (10 mm by 2 mm rectangle, ~200 μJ/cm²). Ions are accelerated and detected by a time of flight mass spectrometer, and signals are recorded and averaged typically for 2500 laser shots by a digital storage oscilloscope (Tektronix TDS5032B).

B. Calculational

Neutral, cationic, and anionic niobium clusters have been investigated by DFT calculations of their structures,30–33 binding energies,30 and reaction pathways.34,35 In this study, calculations include geometry optimizations, vibrational frequency determination for the neutral Nbₙ cluster, related Nbₙ/CO/H₂ adsorption clusters, and the transition states of the reaction pathway. These DFT calculations are performed employing Becke’s exchange36 and Perdew-Wang correlation37 functional, denoted as BPW91, within the GAUSSIAN 03 package.38 The LANL2DZ basis set, which involves the Los Alamos effective core potential plus a double zeta basis set, is employed to model the niobium atom, and the standard 6-311+G(2d, p) basis set has been used to model carbon, oxygen, and hydrogen atoms. All calculations are carried out with the GAUSSIAN 03 program.38

III. RESULTS

A. Reactions of Mₙ with CO+H₂

Mass spectra for the neutral Nbₙ cluster distribution (n=7–10), reactions of Nbₙ clusters (n=7–10) with 50 ppm CO, 1.5% H₂, and 92 ppm CO+0.2% H₂ in a flow tube reactor are shown in Fig. 1. In Fig. 1(a), the mass spectrum of bare metal Nbₙ (n=7–10) clusters is presented. Some carbide and oxide clusters are observed in the mass spectrum because carbon and oxygen impurities are difficult to remove in our experiments, even if high purity helium carrier gas
(99.995%) is employed for the expansion. For the reaction of Nbₙ clusters with 50 ppm CO, primary and secondary adsorption products, NbₙCO and Nbₙ(CO)₂, are both detected for n ≥ 3; only the n = 7–10 cluster range is plotted in Fig. 1(b). With a 1.5% H₂/He gas mixture added to the flow tube reactor, one or more hydrogen molecules can adsorb on the Nbₙ clusters for n ≥ 3 and n ≠ 8 and 10, as seen in Fig. 1(c). Nb₈ and Nb₁₀ are inert in the reaction with H₂ under these experimental conditions. Reaction of Nbₙ clusters with a mixture of CO and H₂ yields observed products NbₙH₂ₖ (n = 3 and n ≠ 8 and 10, k = 1, 2, 3, …) and NbₙCOH₂ₖ (n = 3 and n ≠ 10, k = 1, 2, 3, …), as shown in Fig. 1(d). Note that a relatively intense mass peak around the Nb₈ cluster is identified as Nb₈COH₄.

Mass spectra for the reaction of Nbₙ (n = 7–10) with 92 ppm CO+5%, 1%, and 0.2% H₂ are presented in Fig. 2. Nb₈COH₄ is always much stronger than its neighbor peaks Nb₈COH₂ₖ (k = 1, 3, 4, …) when H₂ concentration changes.
from 0.2% to 5%; however, other Nbₙ (n ≥ 3 and n ≠ 8 and 10) clusters adsorb more hydrogen molecules as the hydrogen concentration is increased. For example, the strongest signal switches from Nb₇COH₂ to Nb₇COH₆ as the H₂ concentration is increased from 0.2% to 5%, as shown in Figs. 2(c) and 2(a). Because Nb₇COH₄ has the same mass number as a Nb₈O₂ impurity, pure helium gas is injected in the flow tube reactor as a reference; the Nb₈O₂ signal contribution is negligible.

Mass spectra for the reaction of Mₙ (M = V, Nb, and Ta, n = 7–10) clusters with 92 ppm CO+0.2% H₂ in a flow tube reactor are plotted in Fig. 3. Mass resolution for Taₙ clusters in Fig. 3(a) is reduced due to the high mass of Ta₉ clusters (1267 amu for Ta₇ and 1810 amu for Ta₉) compared to that of Vₙ or Nbₙ clusters. Hydrogen molecule adsorption products on Mₙ and MₙCO (M = V and Ta, n = 3) clusters are observed, and V₈,10 clusters show low reactivity toward H₂. For other clusters, no size dependent behavior is identified, as shown in Fig. 3. These observations are different from those for reaction of H₂ with Nb₉ and Nb₉O₂, presented in Fig. 1(d).

**B. Reaction of Mₙ with CH₃OH**

Product yields for Mₙ (M = V, Nb, and Ta) reacting with CH₃OH/He in a flow tube reactor are displayed in Fig. 4. Mass resolution in Fig. 4(c) is low due to the high mass of Taₙ clusters. In the reaction of Nbₙ with CH₃OH, primary and secondary adsorption products are fully dehydrogenated to form NbₙCO and Nbₙ(CO)₂ for n = 3 and n ≠ 8 and 10. For the Nb₁₀ cluster, only nondehydrogenated products are detected as Nb₁₀COH₄/Nb₁₀CH₃OH and Nb₁₀(COH₄)₂/Nb₁₀(CH₃OH)₂ in our experiment. For the Nb₉ cluster, both nondehydrogenated products Nb₉COH₄/Nb₉CH₃OH and Nb₉(COH₄)₂/Nb₉(CH₃OH)₂ and fully dehydrogenated products Nb₉CO and Nb₉(CO)₂ are observed simultaneously in mass spectra shown in Fig. 4(b). Fully dehydrogenated products MₙCO and Mₙ(CO)₂ (n = 3–11) are only identified in the reaction of Vₙ and Taₙ clusters with CH₃OH, as seen in Figs. 4(a) and 4(c). For the reaction of V₉, Nb₉, and Ta₉ (n = 3–11) clusters with CH₃OH, nondehydrogenated products are only observed for Nb₉ and Nb₁₀; all other clusters in this study yield fully dehydrogenated product clusters.

**C. Pickup cell experiments**

Reactions of Mₙ (M = V, Nb, and Ta) with mixed gases CO+H₂ in a pickup cell are also explored. Only CO adsorbed products MₙCO are observed for all the pickup cell experiments. Note that Nb₁₀CO is relatively weaker than other NbₙCO (n ≠ 10) products, as observed by Holmgren et al.\(^{23}\) MₙCO (M = V, Nb, and Ta) clusters are the only observed products for reactions of Mₙ with CH₃OH in the pickup cell. These species are fully dehydrogenated from MₙCH₃OH clusters. No product is detected for the Nb₁₀ cluster.

**IV. DISCUSSION**

**A. Reaction of Nbₙ clusters with CH₃OH**

Three types of reactions are identified for the interaction of Nbₙ cluster with CH₃OH in the flow tube reactor experiments presented in Fig. 4(b). First, fully dehydrogenated...
products Nb₈CO are detected for \( n \geq 3 \) and \( n \neq 8 \) and 10. Second, for \( n = 10 \), only the nondehydrogenated product Nb₁₀CH₃OH/Nb₁₀COH₄ is observed. Third, for \( n = 8 \), both dehydrogenated and nondehydrogenated products are detected simultaneously, such as Nb₈CO/CNb₈O and Nb₈CH₃OH/Nb₈COH₄. This size dependent behavior indicates the diverse dehydrogenation barriers existing for the reaction of Nbₙ clusters with CH₃OH, as discussed below for these distinct cases:

1. For \( n = 3–11 \) and \( n \neq 8 \) and 10, detection of fully dehydrogenated products indicates that the barrier for dehydrogenation of intermediate products NbₙCH₃OH must be lower than the initial reactant energy of Nbₙ + CH₃OH. In the flow tube reactor, Nbₙ clusters generated from laser ablation are cooled to \( \sim 300–400 \) K due to a large number of collisions with the helium buffer gas. Therefore, if a high barrier exists for the CH₃OH dehydrogenation on Nbₙ clusters, association products NbₙCH₃OH should be observed in the mass spectrum [Fig. 4(b)]; however, only the fully dehydrogenated products NbₙCO/CNb₈O are detected.

2. For \( n = 10 \), instead of dehydrogenation products, only association products Nb₁₀(CH₃OH)₂ are observed, indicating that the dehydrogenation barriers for Nb₁₀(CH₃OH)₂ must be higher than the initial energy of Nb₁₀ + CH₃OH. On the contrary, neither the association product Nb₁₀CH₃OH nor the dehydrogenated product Nb₁₀CO is observed in the pickup cell experiment. A similar behavior has been found for reaction of Nb₁₀+CO, in that the Nb₁₀CO signal is significantly weaker than the other NbₙCO (\( n \neq 10 \)) signals in the pickup cell experiment, but it is not weaker than the other cluster signals in the flow tube experiment.

These results illustrate that the binding energy between Nb₁₀ and CO is weak and that cooling the Nb₁₀CO association cluster in the flow tube reactor can help us to stabilize the weakly bound product: collisional cooling of intermediates does not occur in the pickup cell. Thus, a weakly bound molecular adsorption cluster between Nb₁₀ and CH₃OH is similar to Nb₁₀CO and can only occur in the flow tube reactor. Dehydrogenation of hydrocarbon compounds on transition metal surfaces must involve a hydrogen atom transfer to a metal atom. Furthermore, a weakly bound association complex indicates a relatively long distance between the associated Nb₁₀ and CH₃OH moieties and a relatively high barrier for hydrogen atom transfer from carbon and/or oxygen to niobium. Thus, only association products are observed for Nb₁₀+CH₃OH in the flow tube experiment.

3. For \( n = 8 \), two peaks, a dehydrogenated product Nb₈CO/CNb₈O and a nondehydrogenated product Nb₈CH₃OH/Nb₈COH₄, are observed in the mass spectrum of Nb₈+CH₃OH, as shown in Fig. 4(b). One can estimate that the dehydrogenation barrier for Nb₈CH₃OH is close to the initial reactant energy of Nb₈ + CH₃OH. In the flow tube experiment, some Nb₈CH₃OH/Nb₈COH₄ intermediates are stabilized through collision with helium gas, and some can surmount the dehydrogenation barrier to produce Nb₈CO/CNb₈O. Consequently, the barrier height for dehydrogenation of CH₃OH on Nbₙ clusters, from high
to low, is suggested to be \(Nb_{10} > Nb_8 > Nb_n\) \((n \neq 8 \text{ and } 10)\).

B. Reaction of \(Nb_n\) clusters with \(CO+H_2\)

The stable species \(Nb_8CH_3OH/Nb_8COH_4\) is observed as a product for the reaction of \(Nb_n\) clusters with \(CO+H_2\). In the flow tube experiment, hydrogen association products \(Nb_kCOH_{2k}\) \((k=1,2,3,\ldots)\) are observed, as shown in Fig. 1(d); however, hydrogen association products with bare metal clusters \(Nb_kH_{2k}\) \((k=1,2,3,\ldots)\) are not detected in either reaction with \(H_2\) [Fig. 1(e)] or with mixture gases \(CO + H_2\) [Fig. 1(d)]. Thus, \(CO\) adsorption on the \(Nb_8\) surface prior to \(H_2\) is suggested because adsorption of \(H_2\) on a \(Nb_8\) cluster has a relatively high barrier or a relatively low desorption energy.\(^{23}\) The electronic structure of \(Nb_8\) is changed by \(CO\) adsorption leading to a decrease of the hydrogen adsorption barrier (lower than the initial energy, \(Nb_8+CO + H_2\)). Therefore, \(Nb_8COH_{2k}\) species are observed in the mass spectrum of Fig. 1(d). An intense mass peak, \(Nb_8COH_4\), identified in the mass spectra in Figs. 1(d) and 2, is always stronger than its neighbor mass peaks \(Nb_8COH_2\) and \(Nb_8COH_4\) under the condition of different hydrogen concentrations in the flow tube reactor. This behavior is different from that of other \(Nb\) clusters. For \(n=10\), neither hydrogen association products \(Nb_{10}H_{2k}\) nor \(Nb_{10}COH_{2k}\) are observed due to a weak bond between hydrogen molecules and \(Nb_{10}\) and \(Nb_{10}CO\) or a high adsorption barrier as above for \(Nb_8\). The pickup cell experiment\(^{35}\) suggests that the binding energy of \(Nb_{10}\) with \(CO\) is low and thereby, the chemical behavior of \(Nb_{10}\) and \(Nb_{10}CO\) toward adsorption of \(H_2\) can be expected to be similar. Thus, no \(H_2\) adsorption on \(Nb_{10}\) and \(Nb_{10}CO\) is observed, as shown in Figs. 1(d) and 2. For \(n \geq 3\) and \(n \neq 8\) and 10, one or more hydrogen association products \(Nb_nCOH_{2k}\) \((k=1,2,3,\ldots)\) are observed in our flow tube experiments, as shown in Fig. 1(d), and mass peak intensities of hydrogen rich clusters decrease with the number of adsorbed hydrogen molecules, e.g., \(Nb_8COH_2 > Nb_7COH_4 > Nb_6COH_6\). This observation indicates that the hydrogen desorption is controlled by a kinetic process; this process is also confirmed by the change of \(Nb_8COH_{2k}\) relative intensity with change in \(CO/H_2\) concentration (see Fig. 2). For example, \(Nb_8COH_2\) is the most intense mass peak for low (0.2%) hydrogen concentration, while \(Nb_8COH_6\) is the most intense peak for high (5%) hydrogen concentration in the flow tube reactor. Thus, \(Nb_8COH_4\) is a stable structure, and its formation is controlled by dynamic energetic processes (temperature, barrier, electronic structure,\ldots) rather than by adsorption kinetics. This result is strongly supported by the results of the \(Nb_n\) cluster reactions with \(CH_3OH\), as discussed above.

The product \(Nb_8COH_4\) is observed in mass spectra for the reaction of \(Nb_8\) with \(CO+H_2\), but the structure of \(Nb_8COH_4\) cannot be directly identified. \(Nb_8COH_4\) has several possible structures: (1) \(CH_3OH\) adsorbed on \(Nb_8\), (2) \(CO\) molecularly adsorbed on \(Nb_8\) with four hydrogen atoms dissociatively adsorbed on \(Nb_6\), (3) both \(CO\) and four hydrogen atoms dissociatively adsorbed on \(Nb_8\), (4) \(CO\) dissociatively adsorbed on \(Nb_8\) and four hydrogen atoms dissociatively adsorbed on \(CO\) ligand, and other possibilities. Infrared spectroscopy to detect \(C-H\) and/or \(O-H\) vibrations of \(Nb_8COH_4/Nb_8CH_3OH\) would be a useful method to explore product structure. Unfortunately, infrared multiphoton dissociation experiments do not produce a change in the appropriate mass channels due to very weak signals and/or cross section issues, and \(Nb_8CH_3OH\) \((Ar)_n\) neutral clusters apparently do not form in our experiments because these clusters are too hot for weak van der Waals bonds to form and stabilize.

C. Mechanism of methanol formation on \(Nb_8\) cluster: DFT calculations

The observation of a stable \(Nb_8COH_4\) product in both reactions of \(Nb_8+CO+H_2\) and \(Nb_8+CH_3OH\) suggests that \(CH_3OH\) can be generated on \(Nb_8\) by the following reaction \((\Delta_H=-1.05\text{ eV based on DFT calculations})\) presented below and in Fig. 5:

\[
\text{Nb}_8 + CO + 2H_2 \rightarrow \text{Nb}_8COH_4 \rightarrow \text{Nb}_8 + CH_3OH.
\]

DFT calculations are performed at the BPW91/LANL2DZ/6-311+G\((2d,p)\) level to explore the possibility of \(CH_3OH\) formation on a \(Nb_8\) cluster through reaction (2). In these DFT calculations, the lowest spin states of all calculated structures of the \(Nb_8\) cluster and intermediates are singlets. To have an idea of the validity of the adopted DFT method and basis function, Table I summarizes some calculated and available experimental adiabatic ionization energies of \(Nb_n\) and related clusters \(Nb_nCO/CNb_nO\) \((n=3\text{ and } 8)\). The adiabatic ionization energies for \(Nb_3\) and \(Nb_8\) clusters are 5.88 and 5.35 eV, which are in good agreement with experimental data of 5.81 and 5.48 eV, respectively. Our calculational results are better than those obtained at the B3P86/LANL2DZ level.\(^{34}\) For the dissociatively adsorbed CO cluster CNb_8O, the ionization energy is predicted to be 6.03 eV, also in agreement with 5.82±0.02 eV as measured by photoionization efficiency spectroscopy.\(^{34}\) The calculated binding energies of CO with \(Nb_3\) are larger by 0.64–0.90 eV at the B3P86/LANL2DZ level than those at the BPW91/LANL2DZ/6-311+G\((2d)\) level, as listed in the last column of Table I.

The potential energy surface profile for \(CH_3OH\) formation from \(CO+H_2\) on neutral \(Nb_8\) clusters is shown in Fig. 5. The structures of intermediates and transition states on this surface are schematically shown in Fig. 6. The minima connected by a given transition state are confirmed by intrinsic reaction coordinate calculations as manipulated in the GAUSSIAN 03 program. As shown in Fig. 5, the first step, molecular adsorption of CO on the \(Nb_8\) cluster to form \(Nb_8CO\), is an exothermic reaction. Via transition state TS0, the molecular adsorption product \(Nb_8CO\) can transform to a dissociative adsorption product \(CNb_8O\) (shown by the dash line in Fig. 5). Thus, dissociative adsorption or molecular adsorption strongly depends on the details of the metals and adsorbed molecules.\(^{34,40}\) A \(H_2\) adsorption channel for dissociation of one hydrogen molecule on \(Nb_8\) and formation of \(Nb_8HH(CO)\) is available, and a more favorable pathway with \(H_2\) molecules is present in the reaction. Therefore, dis-
sociative adsorption of CO on Nb₈ cluster will be inhibited for the reaction of Nb₈ with CO+H₂.

Molecular adsorption of CO on the Nb₈ cluster allows CH₂OH to be formed on Nb₈ through reaction with CO +2H₂, as illustrated by the solid lines connecting transition states TSₓ (x=1, 2, 3, and 4) and reaction intermediates in Fig. 5. After molecular adsorption of CO, one hydrogen atom transfer from the Nb₈ moiety to the CO ligand, one by one, by surrounding transition states TS₁ and TS₂, and Nb₈(CH₂O) is formed. Subsequently, another adsorbed hydrogen molecule is dissociated on the Nb₈(CH₂O) cluster, and one hydrogen atom transfers to the CO ligand and another one still stays on the Nb₈ moiety. A stable intermediate Nb₈HH(CH₂O) (2.75 eV lower than the initial energy) is formed, as shown in Figs. 5 and 6. The transfer of the last H atom leads to Nb₈(CH₂OH) via TS₄ and finally generates product Nb₈+CH₃OH. Based on DFT calculations, the overall reaction of Nb₈ +CO+2H₂ → Nb₈+CH₃OH is barrierless and thermodynamically favorable. Free CH₂OH molecules cannot be detected by single photon ionization from a 193 nm laser—the ionization energy of CH₂OH is ~10.84 eV.⁴¹

The key step for methanol formation on neutral Nb₈ clusters is that CO must be molecularly adsorbed on the Nb₈ cluster surface. If CO were to dissociate rapidly on the clusters to form CNb₈O before collision with hydrogen molecules, recombination of carbon and oxygen atoms would not be possible, and transfer of hydrogen atoms to form methanol could not occur. Thus, the CO dissociation rate constant on the clusters is an essential parameter for the formation of methanol. According to Rice-Ramsberger-Kassel-Markus (RRKM) theory, the dissociation reaction rate constant for Nb₈CO → CNb₈O is given by

$$k_{\text{dis}} = \nu(1 - E_0/E)^{3/2},$$

in which ν is the effective frequency of the Nb₈CO dissociation coordinate vibration (ν=3×10¹² s⁻¹, ~ 100 cm⁻¹ is assumed), S (intermolecular degrees of freedom) =3n−6, E₀ is the activation energy, E is the total energy E=E₀+E_v+E_a+ΔE, where E_v is the center of mass kinetic energy (~0.3 eV), and E_a is the vibrational energy, given by (3n−6)kT_v. A vibrational temperature of 350 K (reasonable for the flow tube reactor) is assumed. For Nb₈ cluster, E₀ =1.48−0.14=1.34 eV and E=E₀+0.3+0.72=2.50 eV, as shown in Fig. 5. Based on the RRKM calculation, the reaction rate constant kₐ=6.41×10⁴ s⁻¹, and the lifetime of the transition state (tₙ=1/kₐ) is around 15.6 ps. These results indicate that CO remains molecularly adsorbed on Nb₈ cluster surface and the intermediate Nb₈CO can undergo many collisions with hydrogen molecules before CO dissociates on the cluster. Consequently, hydrogen molecules are adsorbed and a potential reaction pathway for methanol formation is displayed in Fig. 5.

The CO dissociation rate constants on Nb₃, Nb₄, and Nb₇ are likewise calculated as 3.18×10¹⁰, 3.71×10¹⁰, and 5.41×10⁷ s⁻¹, respectively, as listed in Table II. Note that the rate constants k₃, k₄, and k₇ are much larger than k₈, which suggests that CO is rapidly dissociated (within nanoseconds) to CNb₈O on the Nb₈ clusters (n=3, 4, and 7) prior to collision with H₂/He. Thus, methanol formation is suppressed.

TABLE I. Adiabatic ionization energies (IEs) and binding energies of neutral Nb₈, Nb₃CO, CNb₈O, Nb₈, Nb₃CO, and CNb₈O, as calculated by BPW91/LANL2DZ/6-311+G(2d,f).

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Calc. IE (eV)</th>
<th>Expt. IE (eV)</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₈</td>
<td>5.88/6.8⁴</td>
<td>5.81⁵</td>
<td>...</td>
</tr>
<tr>
<td>Nb₃CO</td>
<td>5.46/6.6⁴</td>
<td>...</td>
<td>1.96/2.60⁹</td>
</tr>
<tr>
<td>CNb₈O</td>
<td>6.03/6.8⁴</td>
<td>5.82⁺</td>
<td>2.89/3.79⁺</td>
</tr>
<tr>
<td>Nb₇</td>
<td>5.35</td>
<td>5.48⁹</td>
<td>...</td>
</tr>
<tr>
<td>Nb₃CO</td>
<td>5.26</td>
<td>...</td>
<td>1.45</td>
</tr>
<tr>
<td>CNb₈O</td>
<td>5.34</td>
<td>...</td>
<td>2.28</td>
</tr>
</tbody>
</table>

⁴Reference 34.
⁵Reference 39.
on Nb₈ (n ≠ 8) cluster surfaces as CO can dissociate on these clusters before the Nb₈CO intermediate can adsorb a hydrogen molecule. In addition, as seen from Table II, the association energy of Nb₈CO is estimated at 1.23 eV (lower than for other clusters), and the Nb₈CO bond is the weakest of all those calculated. This trend is in good agreement with the literature²⁵,³⁰ and our experimental results.

While proving a negative, that is, that Nb₈ (n ≠ 8) does not support the reaction CO+2H₂→CH₃OH, it is notoriously difficult, the above calculations and discussion point out that the path chosen for Nb₈ to generate methanol from CO and H₂ is not readily available to clusters of similar size (n = 3–10 and n ≠ 8).

Additionally, no obvious systematic, size dependent behavior is observed for the reactions of Mₙ (M=V and Ta) with CO+H₂ and CH₃OH. For reactions of Vₙ and Taₙ clusters with CH₃OH, all adsorbed products are fully dehydrogenated; this means that the dehydrogenation barriers for such reactions are lower than the initial energies for Mₙ +CH₃OH. No special mass peak for MₙCOH₄ (M=V and Ta) is observed for reactions of Vₙ and Taₙ clusters with CO+H₂, either in the flow tube reactor or pickup cell. As can be surmised from Fig. 5, other metal clusters (Mₙ=Vₙ, Nbₙ, and Taₙ, but Mₙ ≠ Nb₈) do not form CH₃OH in such a reaction because the hydrogen transfer barriers for MₙCO are probably too high. Additionally, if the hydrogen transfer barriers are relatively low and some CH₃OH is formed on Mₙ clusters, MₙCH₃OH should readily dehydrogenate to MₙCO/CH₃O due to the low dehydrogenation barriers.

V. CONCLUSIONS

Reaction of CO with H₂ on neutral Vₙ, Nbₙ, and Taₙ clusters in the gas phase is explored by employing a flow tube reactor and a time of flight mass spectrometer with 193 nm single photon ionization. A strong size dependent reactivity of Nbₘ toward CO, H₂, and CH₃OH is characterized. A stable product Nb₈COH₄ is identified for reactions of both Nb₈+CO+H₂ and Nb₈+CH₃OH, which suggests that CH₃OH is formed on the Nb₈ cluster through reaction of Nb₈+CO+2H₂. Furthermore, theoretical DFT calculations indicate that the reaction of Nb₈+CO+2H₂→Nb₈+CH₃OH is barrierless and thermodynamically and kinetically favorable. According to our DFT calculations, stable structures are formed for Nb₈HH(CH₂O), Nb₈H(CH₃O), and Nb₈(CH₃OH) species on the reaction potential energy surface. For all other Vₙ, Nbₙ (n ≠ 8), and Taₙ clusters, either the hydrogen transfer barrier is high so that CH₃OH formation does not occur or the hydrogen transfer barrier is low enough so that CH₃OH is formed, but it is not preserved on the clusters due to a low dehydrogenation barrier.

ACKNOWLEDGMENTS

This work was supported by the U.S. DOE BES Program and the NSF ERC for Extreme Ultraviolet Science and Technology under NSF Award No. 0310717.

TABLE II. CO dissociation barriers and reaction rate constants on Nb₈ cluster surface, as calculated by BPW91/LANL2DZ/6-311+G(2d). Energies are in eV and relative to the initial energy (Nb₈+CO).

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Nb₈CO/E</th>
<th>TS0/E</th>
<th>kₚ (s⁻¹)²</th>
<th>τₚ (s)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₁</td>
<td>1.99</td>
<td>0.88</td>
<td>3.18×10¹⁰</td>
<td>3.15×10⁻¹¹</td>
</tr>
<tr>
<td>Nb₄</td>
<td>1.81</td>
<td>0.43</td>
<td>3.71×10⁸</td>
<td>2.70×10⁻₉</td>
</tr>
<tr>
<td>Nb₇</td>
<td>1.66</td>
<td>0.57</td>
<td>5.41×10⁷</td>
<td>1.85×10⁻₈</td>
</tr>
<tr>
<td>Nb₈</td>
<td>1.48</td>
<td>0.14</td>
<td>6.41×10⁴</td>
<td>1.56×10⁻⁵</td>
</tr>
<tr>
<td>Nb₁₀</td>
<td>1.23</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>

²Association energy.
³Transition state energy for Nb₈CO to CNb₈O.
⁴Calculated reaction rate constant.
⁵Transition state lifetime τₚ=1/kₚ.
34M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 03, revision C.02, Gaussian, Inc., Wallingford, CT, 2004.