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**Probing the Microhydration of Metal Carbonyl: A Photoelectron
Velocity-Map Imaging Spectroscopic and Theoretical Study of
 $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$**

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Abstract:

A series of microhydrated nickel carbonyls, $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$), are prepared via a laser vaporization supersonic cluster source in the gas phase and identified by mass-selected photoelectron velocity-map imaging spectroscopy and quantum chemical calculations. Vertical detachment energies for the $n = 1-4$ anions are measured from the photoelectron spectra to be 1.429 ± 0.103 , 1.698 ± 0.090 , 1.887 ± 0.080 , and 2.023 ± 0.074 eV, respectively. The C–O stretching vibrational frequencies in the corresponding neutral clusters are determined to be 1968, 1950, 1945, and 1940 cm^{-1} for $n = 1-4$, respectively, which are characteristic of terminal CO. It is determined that the hydrogen atom of the first water molecule is bound to the nickel center. Addition of a second water molecule leads to solvation at the carbonyl terminal. The formation of a water-ring network is achieved via a water trimer and is perfected at the tetramer. Spectroscopy combined with theory suggests that the water molecules prefer to antisymmetrically solvate the carbonyl terminals. The present findings would have important implications for fundamental understanding of the multifaceted mechanisms of the multibody interaction of water and carbon monoxide with transition metals.

Introduction

The study of the interaction of carbon monoxide with metal atoms, clusters and surfaces is of considerable interest because of its importance in modern coordination chemistry, heterogeneous and homogeneous catalysis, inorganic, and organometallic synthesis.^{1,2} Various kinds of experimental and theoretical methods have been employed to understand the metal–ligand bonding nature and the binding at active sites of catalysts.^{3–6} For instance, bonding energies of transition metal (TM) carbonyls were measured using collision-induced dissociation.^{7–9} Raman spectroscopy and infrared spectroscopy have been employed to study various charged and neutral metal carbonyls in both rare gas matrices and condensed phase environments.^{10–15} Photoelectron spectroscopy has been used to investigate mass-selected TM carbonyl anions and revealed much useful information of electronic structures.^{16–20} Infrared photodissociation spectroscopy has been successfully applied to probe the structures and C–O stretching vibrational frequencies of TM carbonyl clusters.^{21–23} The series $\text{Ni}(\text{CO})_4 \rightarrow \text{Fe}(\text{CO})_5 \rightarrow \text{Cr}(\text{CO})_6$ represents well-known 18-electron neutral carbonyls.

In contrast with extensive explorations of metal carbonyls, little information is available about how the water molecules solvate metal carbonyls. This issue plays an important role in mechanistic understanding of the multibody interaction of water, carbon monoxide, and metal, which is directly relevant to the industrial process - in particular for the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) involved in many proposed future technologies for energy conversion (e.g., coal conversion to liquid fuels). When water interacts with a metal carbonyl, an energetic competition exists between hydrogen bonding among adjacent water molecules and bonding with metal and/or carbonyl terminal. This raises a fundamental question of how a metal carbonyl is stepwise solvated by adding one water molecule at a time. However, it is difficult to extract such information from the bulk measurements. Here, we use mass-selected photoelectron velocity-map imaging spectroscopy of hydrated nickel carbonyls $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ clusters together with quantum chemical calculations to generate a microscopic view for the stepwise microhydration of metal carbonyl. Experimental and theoretical results reveal that the water molecules prefer to form a water-ring network and anti-symmetrically solvate the carbonyl terminals.

Methods

Experimental setup

The experiments are carried out using an instrument with a laser vaporization source, a time-of-flight (TOF) mass spectrometer, and a collinear velocity-map photoelectron imaging analyzer. The apparatus has been previously described in detail.²⁴ Briefly, the $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ complexes are generated directly from the laser vaporization process in expansions of a mixed CO–H₂O gas seeded in helium using a pulsed General Valve (0.8 mm nozzle). A mixed CO–H₂O gas is obtained by flowing 10% CO/He at pressure of 3 atm through a reservoir containing liquid water at room temperature. The free expansion is skimmed into a second chamber where negative ions are extracted perpendicularly by a -1.2 kV high pulse voltage and analyzed by the TOF mass spectrometer. After separation in space, the anionic clusters of interest are mass selected into the photodetachment region and crossed with a laser beam. 355 nm (3.496 eV) photon energy is used for the photodetachment of these anionic clusters. Photoelectrons are analyzed by the collinear velocity-map photoelectron imaging analyzer, which is built according to a modified design of Eppink and Parker.²⁵ The electrons are mapped onto an image detector consisting of a microchannel plate (MCP) assembly and a phosphor screen. The positions of photoelectrons are recorded by a charge-coupled device (CCD) camera and one typical image is obtained by accumulating 50000-100000 laser shots at 10 Hz repetition rate. The spectrometer is calibrated using the spectra of Ag^- and Au^- at 355 nm. The energy resolution is better than 5%, corresponding to 50 meV at electron kinetic energy (eKE) of 1 eV. The uncertainties of the experimental detachment energies are mainly caused by the restriction of this resolution. They are estimated by the product of the energy resolution and the kinetic energy of corresponding photoelectrons.

Computational details

The TURBOMOLE V6.4 program is used for all calculations.²⁶ A series of density functional theory methods, i.e. B3LYP, B3LYP, BLYP, BP86, PBE, PBE0, TPSS, and TPSSH are tested for the $n = 1$ cluster, which are summarized in Table S1 in the Electronic Supplementary Information (ESI). It can be found that the B3LYP/def2-TZVP method yields better agreement with experiment than others, hence this method is accordingly employed for the present calculations. Structures are optimized until Cartesian gradients are smaller than 1×10^{-5} Hartree/Bohr and the energy change is smaller than 1×10^{-6} Hartree. The SCF convergence criterion is 1×10^{-7} Hartree for the energy and 1×10^{-7} a.u. for the RMS of the density. Harmonic vibrational frequency

analyses are carried out to confirm that the structures are real minima. Relative energies include zero-point vibrational energies. Carbonyl stretching frequencies are scaled by a factor of 0.969, which is determined by the ratio of the experimental value (2143 cm^{-1}) to the B3LYP/def2-TZVP one (2212 cm^{-1}) of free CO molecule. The theoretical vertical detachment energy (VDE) is computed as the difference in energy between the optimized anion and neutral species both at the anionic optimized geometry, and the theoretical adiabatic detachment energy (ADE) is calculated as the difference in energy between the optimized anionic and neutral species.

Results and discussion

Photoelectron spectroscopy

Photoelectron imaging results of $\text{Ni(CO)}_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$) at 355 nm (3.496 eV) are shown in Fig. 1. The raw images (black background) collected in the experiments indicate the projection of the 3D laboratory frame photoelectron probability density onto the plane of the imaging detector, and the reconstructed images (purple background) represent the central slice of the 3D distribution from its 2D projection. The direction of laser polarization is indicated by a double arrow on each raw image. The experimental VDE of each cluster anion is measured from the maximum of band X in the respective 355 nm spectrum, and the ADE is estimated by drawing a straight line along the rising edge of band X and then adding the instrumental resolution to its intersection with the binding energy axis, which are summarized in Table 1.

The photoelectron spectrum of Ni(CO)_3^- shows three resolved features (Fig. 1). The first peak at 1.104 ± 0.120 eV designates the VDE (Table 1), and the others correspond to the vibrational progression of the neutral. The ADE is determined to be 1.023 ± 0.124 eV, which is in agreement with the value of 1.077 ± 0.013 eV reported previously.²⁷ The vibrational frequency of Ni(CO)_3 is estimated to be 2030 ± 320 cm^{-1} (Table 2), characteristic of C-O stretch, which is close to the matrix IR measurement ($\nu_{\text{C-O}} = 2017$ cm^{-1} in argon,¹⁰ 2025 cm^{-1} in neon¹²).

Upon solvation by one H_2O molecule, the spectrum of $\text{Ni(CO)}_3(\text{H}_2\text{O})^-$ shifts to a higher electron binding energy by 0.325 eV relative to that of bare Ni(CO)_3^- and has two resolved peaks. The VDE and ADE is measured to be 1.429 ± 0.103 and 1.290 ± 0.110 eV, respectively. The peak at 1.689 eV is due to the C-O stretch of $\text{Ni(CO)}_3(\text{H}_2\text{O})$, which vibrational frequency is evaluated to be 1968 ± 270 cm^{-1} (Table

2). When the second solvated H₂O molecule is added, the VDE of Ni(CO)₃(H₂O)₂⁻ is increased by 0.269 eV with respect to that of $n = 1$. The ADE and C-O stretching vibrational frequency is estimated to be 1.507 ± 0.099 eV and 1950 ± 240 cm⁻¹, respectively. The photoelectron spectrum of $n = 3$ and 4 continues to shift to higher electron binding energy at 1.887 ± 0.080 and 2.023 ± 0.074 eV (Table 1), respectively, which gives the ADE of 1.647 ± 0.092 and 1.736 ± 0.088 eV.

As a summary of the experimental results, the VDE of Ni(CO)₃(H₂O) _{n} ⁻ increases as n changes from 0 to 4, implying that the negative electron is stabilized upon solvation by H₂O molecules. The characteristic bands become appreciably broader with the increase of cluster size but without any dramatic change in contour of the electron detachment features, suggesting that the water molecules have little effect on the Ni(CO)₃ substrate.

Comparison between experimental and theoretical results

Quantum chemical calculations are performed to elucidate the geometric and electronic structures of Ni(CO)₃(H₂O) _{n} ⁻ and support the spectral assignments. **None of the quartet anions are found to be energetically competitive with the corresponding doublet isomers (*vide infra*). Only the results from the representative low-lying isomers with the doublet electronic state are presented.** Optimized structures of Ni(CO)₃(H₂O) _{n} ⁻ ($n = 0-4$) anions are shown in Fig. 2. The comparison of experimental VDEs and ADEs to the calculated values is given in Table 1. Experimental and calculated CO stretching vibrational frequencies of neutral Ni(CO)₃(H₂O) _{n} ($n = 1-4$) complexes are reported in Table 2.

The bare Ni(CO)₃⁻ anion (labeled **0A**) is calculated to have a D_{3h} symmetry with a ²A₂' ground state, in which all carbonyl ligands are terminally bonded to the nickel atom (Fig. 2), consistent with the previous work.¹⁰ The theoretical VDE and ADE is 1.083 and 0.931 eV agrees well with the experimental value of 1.104 and 1.023 eV, respectively (Table 1). The density functional calculation for CO stretching vibrational frequency of neutral Ni(CO)₃ (2033 cm⁻¹) also supports the experimental observation (2030 cm⁻¹).

The structure of Ni(CO)₃(H₂O)⁻ (labeled **1A**) is predicted to have a C_s symmetry with a ²A' ground state, in which one water hydrogen atom is bonded to the nickel center along the C_3 axis (Fig. 2). Optimization of the initial structure with the water

molecule hydrogen-bonded to the oxygen atom of CO converges to isomer **1A**. The structure with a quartet electronic state lies higher in energy by 2.329 eV above **1A**. The VDE and ADE for $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})^-$ (**1A**) is calculated to be 1.505 and 1.322 eV, respectively, which is in excellent agreement with the corresponding experimental value of 1.429 and 1.290 eV (Table 1). As listed in Table 2, the calculated CO stretching vibrational frequency of neutral $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})$ (1979 cm^{-1}) is consistent with the experimental value (1968 cm^{-1}).

For the $n = 2$ cluster, the lowest-lying isomer, labeled **2A**, is a C_1 structure with a ^2A ground state, in which the second water forms one water–water hydrogen-bond and one water–O hydrogen-bond (Fig. 2). The **2B** isomer lies higher in energy by 0.052 eV, in which each water is singly bonded to the nickel atom. The simulated VDE of **2A** (1.836 eV) agrees better with experiment (1.698 eV) than that of **2B** (Table 1). The agreement of ADE and CO stretching vibrational frequency is also obtained.

In the lowest-lying isomer of the $n = 3$ cluster, **3A**, the three waters form a three-membered ring, as shown in Fig. 2. The next energetically higher isomer (**3B**, +0.036 eV) consists of a C_1 structure with a ^2A ground state, in which one water molecule is bonded to the nickel atom and two water molecules are hydrogen-bonded to the first water molecule and two CO molecules. The **3C** isomer lies +0.058 eV higher above **3A** and has two waters located on one side of $\text{Ni}(\text{CO})_3$ plane and one water on another side of $\text{Ni}(\text{CO})_3$ plane. The simulated VDE of **3A** (1.969 eV) agrees better with experiment (1.887 eV) than those of **3B** (2.146 eV) and **3C** (2.183 eV) (Table 1). Present calculations also reproduce the ADE and CO stretching vibrational frequency.

For the $n = 4$ cluster, the formation of a four-membered water ring is completed in the most stable structure (**4A**). The **4B** isomer is derived from **3A** by adding the fourth water onto the three-membered ring and one CO terminal, which is located above **4A** by +0.131 eV. In the **4C** isomer (+0.174 eV), the four waters are equally distributed on both sides of $\text{Ni}(\text{CO})_3$ plane and form water–water hydrogen-bonds. The **4D** isomer (+0.209 eV) consists of three waters located on one side of $\text{Ni}(\text{CO})_3$ plane and one water on another side. As compared in Table 1, the simulated VDE of isomer **4A** (2.099 eV) is in good agreement with the experimental VDE value of 2.023 eV, whereas those of isomers **4B-4D** (2.252, 2.480, and 2.476 eV) are much higher than the experimental value.

Frank-Condon (FC) simulations are carried out for the small clusters, $n = 0$ and

1, to further confirm the spectral and structural assignments using the PESCAL program.²⁸ The FC simulated spectrum is shown as blue curve in Figure S3, while wine curve represents the experimentally observed one. The black sticks represent the relative intensities of individual vibrational transitions revealed by simulations. It can be found that the FC simulations reasonably reproduce the overall patterns of experiment, supporting the current quantum chemical calculations.

Discussion

The agreement between the experimental and simulated results allows for establishing the structural evolution of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$. For $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})^-$, the water hydrogen atom is bonded to the nickel center, which is supported by natural population analysis (see Table S2 in the ESI). It has been found that the negative charge mainly resides on the nickel atom, which is manifested by the picture for the spin density isosurface (see Fig. S1 in the ESI). This solvation feature of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})^-$ is different from the $\text{Ni}(\text{H}_2\text{O})^+$ cations,²⁹ in which the water oxygen atom is bound to the nickel center because of the charge-dipole interaction. The water molecule starts to solvate the carbonyl terminal at $n = 2$. The formation of a water-ring network is achieved at $n = 3$ and is perfected at $n = 4$, which is consistent with the converged trend of CO stretching vibrational frequencies as shown in Table 2. It can be concluded that during the sequential solvation process of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$, the water molecules prefer to form a hydrogen-bonding network and antisymmetrically solvate the carbonyl terminals. As shown in molecular orbital pictures (see Fig. S2 in the ESI), LUMO and HOMO consists of the π orbitals localized on the $\text{Ni}(\text{CO})_3$ substrate.

Topological parameters of the $\text{OH}\cdots\text{OH}_2$ and $\text{OH}\cdots\text{OC}$ hydrogen-bonds at bond critical points (BCP) are calculated to assess the competition between hydrogen-bonding among adjacent water molecules and bonding of water molecules to substrates. Electron densities at the bond critical points in the two lowest-lying isomers are given in Table 3. In the **2A** isomer, the electron density of $\text{OH}\cdots\text{OH}_2$ hydrogen-bond (0.02452) is remarkably larger than that of $\text{OH}\cdots\text{OC}$ hydrogen-bond (0.00901), indicating that hydrogen-bonding among adjacent water molecules is much stronger than bonding of water molecules to substrates. Such feature holds true in the larger clusters (Table 3). The average value for electron density of $\text{OH}\cdots\text{OH}_2$

hydrogen-bond (0.02434) in the **3A** isomer is larger than that in the **3B** isomer (0.02149), suggesting that the hydrogen-bonding among adjacent water molecules get stronger when a water-ring network forms. Similar result has also been obtained in the **4A** and **4B** isomers. These findings support the preference of the formation of a water-ring network.

Note that it would be important to study clusters beyond the tetramer. Our calculations indicate that the most stable structure of the $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_5^-$ cluster consists of a five-membered water ring (not shown here), suggesting that a single nickel atom could be able to stabilize the water pentamer. The absence of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ ($n > 4$) clusters here could be due to the warm source in the present experimental conditions. Further improvement in the cluster source via efficient cooling is currently in progress. **Alternatively, mass-selected infrared photon dissociation spectroscopy combined with quantum chemical and molecular dynamics simulation could afford a useful tool for the structural characterization of ion–water complexes in the gas phase.**^{30–36} Such studies have important implications for understanding the nature of the multibody interaction of water and carbon monoxide with transition metals, in particular for the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) involved in many proposed future technologies for energy conversion (e.g., coal conversion to liquid fuels).

Conclusions

Anion photoelectron velocity–map imaging has been combined with quantum chemical calculation to study the electronic structure and chemical bonding of microhydrated nickel carbonyl anions $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$). Vertical detachment energy of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ increases as n changes from 0 to 4, implying that the negative electron is stabilized upon solvation by H_2O molecules. With the increase of cluster size, the characteristic bands become appreciably broader but without any dramatic shift or unexpected change in contour of the electron detachment features. Spectroscopy combined with theory reveals that the hydrogen atom of the first water molecule is bound to the nickel center. Addition of a second water molecule leads to solvation at the carbonyl terminal. The formation of a water-ring network is achieved via a water trimer and is perfected at the tetramer. These findings provide a stepwise picture for molecular-level understanding of the nature of hydrogen-bonding among adjacent water molecules and bonding of water molecules to metal carbonyls.

Electronic Supplementary Information (ESI) available:

Comparison of experimental and calculated VDE values for the most stable isomer of the $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})^-$ anion (**1A**) by different density functional theory methods (Table S1); Natural population analysis results (Table S2); Spin density isosurfaces (Fig. S1); Molecular orbital pictures (Fig. S2); Cartesian coordinates for the isomers.

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Table 1. Comparison of experimental VDE and ADE values (eV) to B3LYP calculated ones for $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$).

Cluster	Isomer	VDE		ADE	
		Calc.	Exp. ^a	Calc.	Exp. ^a
<i>n</i> = 0	0A	1.083	1.104 (120)	0.931	1.023 (124)
<i>n</i> = 1	1A	1.505	1.429 (103)	1.322	1.290 (110)
<i>n</i> = 2	2A	1.836	1.698 (90)	1.532	1.507 (99)
	2B	1.869		1.533	
<i>n</i> = 3	3A	1.969	1.887 (80)	1.405	1.647 (92)
	3B	2.146		1.728	
	3C	2.183		1.597	
<i>n</i> = 4	4A	2.099	2.023 (74)	1.406	1.736 (88)
	4B	2.252		1.427	
	4C	2.480		1.331	
	4D	2.476		1.385	

^a Numbers in parentheses represent the uncertainty in the last digits.

Table 2. Experimental and calculated CO stretching vibrational frequencies of neutral $\text{Ni(CO)}_3(\text{H}_2\text{O})_n$ ($n = 0-4$) complexes.

Species	Calc.	Exp. ^a
Ni(CO)_3	2033	2030 (320)
$\text{Ni(CO)}_3(\text{H}_2\text{O})$	1979	1968 (270)
$\text{Ni(CO)}_3(\text{H}_2\text{O})_2$	1968	1950 (240)
$\text{Ni(CO)}_3(\text{H}_2\text{O})_3$	1947	1945 (215)
$\text{Ni(CO)}_3(\text{H}_2\text{O})_4$	1947	1940 (200)

^a Numbers in parentheses are experimental uncertainties.

Table 3. Electron densities ($\rho(r_b)$, a.u.) of the OH...OH₂ and OH...OC hydrogen-bonds at bond critical points in the two lowest-lying isomers for Ni(CO)₃(H₂O)_{*n*}[−] (*n* = 1-4).

Isomer	OH...OH ₂ hydrogen-bond	OH...OC hydrogen-bond
1A	–	–
2A	0.02452	0.00901
2B	–	–
3A	0.02833 0.02360 0.02109	0.01140 0.00995
3B	0.02150 0.02148	0.00858 0.00851
4A	0.03713 0.03622 0.03054 0.02847	0.01239 0.01193
4B	0.02478 0.02316 0.02214 0.02213	0.00995 0.00740 0.00645

Fig. 1 Photoelectron images of $\text{Ni}(\text{CO})_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$) at 355 nm. The raw image (upper) and the reconstructed image (bottom) after inverse Abel transformation are shown on the left side. The double arrow indicates the direction of the laser polarization. Photoelectron spectra are shown on the right side. **The resolved vibrational structures are labeled with vertical lines.**

Fig. 2 Optimized structures of the $\text{Ni(CO)}_3(\text{H}_2\text{O})_n^-$ ($n = 0-4$) complexes (Ni, blue; C, gray; O, red; H, light gray). Relative energies are given in eV.

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