Observation of H Aggregation onto a Doubly Charged Anion in a Temperature-Controlled Ion Trap

Xue-Bin Wang, Xiao-Peng Xing, and Lai-Sheng Wang


Downloaded from http://pubs.acs.org on February 22, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
Observation of $H_2$ Aggregation onto a Doubly Charged Anion in a Temperature-Controlled Ion Trap

Xue-Bin Wang, Xiao-Peng Xing, and Lai-Sheng Wang*

Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354, and Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352

Received: October 3, 2008; Revised Manuscript Received: October 30, 2008

Hydrogen is the second most difficult gas to be condensed due to its weak intermolecular interactions. Here we report observation of $H_2$ aggregation onto a doubly charged anion, $O_2C(CH_2)_{12}CO_2^-(DC^2-).$ Weakly bound $DC^2-(H_2)_n$ clusters were formed in a temperature-controlled ion trap and studied using photoelectron spectroscopy. The onset of clustering was observed at $30 \text{ K}$, whereas extensive condensation was observed at $12 \text{ K}$ with $n$ up to 12. Photoelectron spectra were obtained for $DC^2-(H_2)_n(n = 0-6)$ at 193 and 266 nm. The spectra of $DC^2-(H_2)_n$ were observed to be identical to that of the bare $DC^2-$ dianion except a slight blue shift, indicating the weak interactions between $H_2$ and the parent dianion. The blue shift on average amounts to $\sim 34 \text{ meV} (3.3 \text{ kJ/mol})$ per $H_2$, which represents the lower limit of the $H_2$ binding energy to $DC^2-$.

Introduction

Molecular hydrogen is an appealing alternative to replace the diminishing fossil fuel as a clean and environmentally friendly energy source. To eventually achieve this goal, one crucial issue is to find economic and efficient hydrogen storage media.1–3 Thus, the study of how molecular hydrogen interacts with a host material has been a recent topic of intensive scientific interests because of the relevance to searching and designing hydrogen storage materials.4–10 Most studies have focused on $H_2$ uptake by bulk storage materials, where heterogeneous phases and multiple components of the medium often complicate interpretation and prevent a microscopic understanding of key controlling factors. Very recently, theoretical investigations have been performed on $H_2$ storage capability of model systems to sort out key factors (van der Waals forces, electrostatic effects, and orbital interactions) that may dictate and influence the $H_2$ binding affinity.11–14

Studies of gas phase clusters containing $H_2$ can provide microscopic insight into interactions of $H_2$ with various substrates and fundamental information relevant to the search of hydrogen storage materials. Numerous gas phase studies of atomic and small metal cluster ions with $H_2$ have been reported.15–26 However, there have been few studies about $H_2$ clustering on complex ions, mainly because of the difficulties to create such $H_2$ solvated clusters, which requires extremely cold environments. Recent advances in ion trap technology have made it possible to produce cold ions at very low temperatures27,28 and to allow spectroscopic studies of gaseous ions under well-controlled temperatures.29–32 In fact, the cold ion trap technique was first demonstrated by generating protonated hydrogen cluster ions $H^+(H_2)_n.28$

Experimental Methods

Here we report observation of $H_2$ aggregation onto a doubly charged dicarboxylate dianion, $O_2C(CH_2)_{12}CO_2^-(DC^2-)$, in a temperature-controlled Paul trap containing a low pressure $H_2$ background gas. The threshold temperature for $H_2$ nucleation was observed to be $\sim 30 \text{ K}$ and extensive aggregation was observed at $12 \text{ K}$, forming $DC^2-(H_2)_n$ clusters with $n$ up to 12. Photoelectron spectra of $DC^2-(H_2)_n(n = 1-6)$ display identical spectral features to that of the parent $DC^2-$ dianion except a very slight increase of the electron binding energies with $n$ (on average of $\sim 34 \text{ meV}$ per $H_2$ molecule) due to the weak van der Waals and electrostatic interactions. Because organic carboxylates are common components in the metal–organic framework hydrogen storage materials,5–10 the current work may be pertinent to understanding the intermolecular interactions of $H_2$ in these promising hydrogen-storage materials.

* To whom correspondence should be addressed. E-mail: ls.wang@pnl.gov.

10.1021/jp808769m CCC: $40.75$ © 2008 American Chemical Society
K, measured by a silicon diode, which was attached to the nearest electrically isolated adaptor made of oxygen-free high purity copper.33 The RF amplitude of the trap was minimized to avoid RF heating.

During the photoelectron spectroscopy (PES) experiment, the DC₂⁻ anions were selected and decelerated before being photodetached in the interaction zone of the magnetic-bottle PES analyzer. Two detachment photon energies were used in the current experiment: 193 nm (6.424 eV) from an excimer laser and 266 nm (4.661 eV) from a Nd:YAG laser. The lasers were operated at a 20 Hz repetition rate with the ion beam off at alternating laser shots for background subtraction. Photoelectrons were collected at nearly 100% efficiency by the magnetic-bottle and analyzed in a 5.2 m long electron flight tube. Time-of-flight photoelectron spectra were collected and converted to kinetic energy spectra, calibrated by the known spectra of I⁻ and ClO₂⁻. The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the respective detachment photon energies. The energy resolution (ΔE/E) of the magnetic-bottle electron analyzer was about 2%, i.e., ~20 meV for 1 eV electrons.

Results and Discussion

Time-of-Flight Mass Spectra. As shown from our previous studies on other dicarboxylate dianions,32,34 a strong mass signal corresponding to the DC₂⁻ dianion was easily observed from our ESI source. As the temperature of the ion trap was lowered, we observed additional peaks in the time-of-flight mass spectra, which became more extensive as temperature was lowered further. Figure 1 displays a few “snapshots” of the mass spectra from 30 to 12 K. The spacing of these extra peaks corresponds to a mass-to-charge ratio of 1, i.e., a mass separation of 2, considering the doubly charged nature of DC₂⁻. This observation suggested that the H₂ molecules used as background gas for collisional cooling in the ion trap began condensing onto the cold doubly charged parent DC₂⁻ to form DC₂⁻(H₂)n clusters. The onset of the H₂ condensation was around 30 K. At the lowest trapping temperature of 12 K, extensive clustering was observed with n up to 12 and essentially no bare DC₂⁻ was left in the ion trap, as shown in Figure 1 (blue).

Photoelectron Spectroscopy. To confirm the identities of these newly formed species and probe the strength of the intermolecular interactions, we obtained the photoelectron spectra of DC₂⁻(H₂)n for n = 0–6 at 193 and 266 nm, as shown in Figure 2. We observed that the spectra of DC₂⁻(H₂)n are identical to those of the parent DC₂⁻ except a small shift to higher binding energies, confirming that these newly formed species at low temperatures are indeed due to weakly bound H₂ clusters. The photoelectron spectra of DC₂⁻ consist of two spectral bands due to detachment from the O lone-pair electrons from the terminal –CO₂⁻ groups, as shown from our previous studies on other similar dicarboxylate dianions.32,34 The current low-temperature spectra were better resolved in comparison to our previous room temperature spectra due to the vibrational cooling. The sharper spectra yielded better defined detachment threshold, from which the adiabatic detachment energy (ADE) was estimated, as given in Table 1 and plotted in Figure 3. The magnitude of the spectral shift induced by each H₂ molecule, defined as ∆ADE(n) = ADE(n) – ADE(n – 1), is also given in Table 1. The ADE increases very slightly with the number of H₂ molecules, ranging from 0.012 to 0.053 eV, due to the very weak van der Waals or electrostatic interactions between H₂ and DC₂⁻.

![Figure 1](image1.png)

**Figure 1.** Temperature-dependent mass spectra of ᴿO₂C(CH₂)₁₂-CO₂⁻(H₂)n. Note the onset of H₂ clustering at 30 K and the increasing aggregation of H₂ with decreasing temperatures. The weak peaks at 71.4 and 73.2 μs in the 30 K spectrum were due to unidentified impurities.

![Figure 2](image2.png)

**Figure 2.** Low temperature photoelectron spectra of ᴿO₂C(CH₂)₁₂-CO₂⁻(H₂)n (n = 0–6) at 193 nm (left) and 266 nm (right).

<table>
<thead>
<tr>
<th>n</th>
<th>ADE (eV)</th>
<th>∆ADE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.503 (10)</td>
<td>0.012 (5)</td>
</tr>
<tr>
<td>1</td>
<td>2.515 (10)</td>
<td>0.053 (5)</td>
</tr>
<tr>
<td>2</td>
<td>2.568 (10)</td>
<td>0.048 (5)</td>
</tr>
<tr>
<td>3</td>
<td>2.616 (10)</td>
<td>0.020 (5)</td>
</tr>
<tr>
<td>4</td>
<td>2.636 (10)</td>
<td>0.039 (5)</td>
</tr>
<tr>
<td>5</td>
<td>2.675 (10)</td>
<td>0.029 (5)</td>
</tr>
<tr>
<td>6</td>
<td>2.704 (10)</td>
<td>0.029 (5)</td>
</tr>
</tbody>
</table>

*All energies are in eV. Numbers in parentheses represent experimental uncertainties in the last digits. Because vibrational structures were not resolved, the ADE was estimated from the 266 nm spectra by drawing a straight line at the leading edge of the threshold spectral band and adding the instrumental resolution to the intersection with the binding energy axis. Previous studies indicated an accuracy of 0.1 eV using this procedure as long as the 0–0 transition was not negligible.29 ∆ADE carries a smaller uncertainty because the spectral shift can be measured more accurately.*

**Table 1: Adiabatic Detachment Energies (ADE) and Incremental Stabilization Energies, ∆ADE = ADE(n) – ADE(n – 1) of ᴿO₂C(CH₂)₁₂-CO₂⁻(H₂)n (n = 0–6)***
The $\Delta ADE(n)$ values shown in Table 1 are not monotonic as a function of $n$: the first $H_2$ gives only a marginal stabilization effect of 12 meV, while the second and third $H_2$ molecules each yield substantially larger effects of ~50 meV. The increase in $ADE$ from further addition of $H_2$ molecules is 20, 39, and 29 meV for $n = 4$, 5, and 6, respectively (Table 1). On average, each $H_2$ molecule induces an increase of ~34 meV to the electron binding energy of $DC^2^-$. $\Delta ADE(n)$ is related to the incremental $H_2$ binding energies (BE) to the $DC^2-$ dianion and the $DC^-$ monoanion: $\Delta ADE(n) = BE[DC^2-(H_2)_n] - BE[DC^-(H_3)_n]$. Because $BE[DC^-(H_3)_n] > 0$, the average $\Delta ADE$ of ~34 meV (3.3 kJ/mol) can be viewed as the lower limit of the $H_2$ binding energy to $DC^2-$. In comparison, we have shown previously that solvation of a dicarboxylate dianion by $H_2O$ induces an increase in $ADE$, ranging from 0.2 to 0.5 eV per $H_2O$ molecule, i.e., the $H$-bonding interaction of $H_2O$ with the dicarboxylate is 1 order of magnitude stronger than the weak interactions by $H_2$.

The $DC^2-$ dianion is quite long with a separation of ~15 Å between the two terminal $-CO_2^-$ groups. It is expected to adopt a linear configuration due to the strong intramolecular Coulomb repulsion (~1 eV), similar to other shorter dicarboxylate dianions that we studied before. We have investigated extensively the solvation of dicarboxylate dianions by $H_2O$ previously and observed that water molecules solvate the two hydrophilic $-CO_2^-$ groups alternately at both ends while avoiding the hydrophobic $-(CH_2)_n-$ backbones. A strong odd—even effect was observed in the $\Delta ADE$ trend because an odd solvent number breaks the equivalence of the two terminal carboxylate groups and only an even number of solvent can solvate both $-CO_2^-$ groups evenly. Thus, an even number of solvent molecules produces a much larger stabilization, which can be roughly viewed as the stabilization of one solvent to one $-CO_2^-$ group. Because of the stronger electrostatic interactions, we expected that $H_2$ should interact with the two terminal $-CO_2^-$ groups in a similar manner. Indeed, we observed that the second $H_2$ produces a much larger stabilization (53 meV) compared to the first $H_2$ (12 meV), suggesting that the first two $H_2$ molecules are bounded to the terminal $-CO_2^-$ groups separately. We expected that the additional $H_2$ molecules should also bind to the $-CO_2^-$ groups in a similar alternating fashion. However, the third $H_2$ produces a stabilization similar to the second $H_2$, breaking the anticipated odd—even pattern. This observation implies that the third $H_2$ is not just interacting with one $-CO_2^-$ at one end. The observed trend of $\Delta ADE(n)$ suggests that for $n \geq 3$ the additional $H_2$ molecules probably begin to interact with the aliphatic backbone via weak van der Waals forces while simultaneously interacting with both terminal charges via charge dipole/quadrupole interactions.

**Conclusions**

In conclusion, we report the observation of aggregation of $H_2$ molecules onto a long-chain doubly charged anion inside a temperature-controlled Paul trap. Photoelectron spectra were obtained for the resulting $DC^2-(H_2)_n$ clusters, revealing the weakly bound nature between $H_2$ and $DC^2-$. The trend of the spectral shift suggests that the first two $H_2$ solvate the two terminal $-CO_2^-$ groups separately while for $n \geq 3$ the additional $H_2$ starts to solvate the aliphatic backbone. The observation of the weakly bound $H_2$ clusters indicates that cold anions can be both produced in and extracted from a Paul trap. The current study shows that $H_2$ interactions with many other complex anions can be investigated using the temperature-controlled Paul trap. In addition, the weakly bound clusters provide new opportunities to allow action spectroscopy to be performed on ultracold complex ions.

**Acknowledgment.** This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Sciences Division and was performed at the EMSL, a national scientific user facility sponsored by DOE’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle.

**References and Notes**

(1) Coontz, R.; Hanson, B. Science 2004, 305, 957.
(3) http://www.eere.energy.gov/hydrogenandfuelcells/.

JP808769M