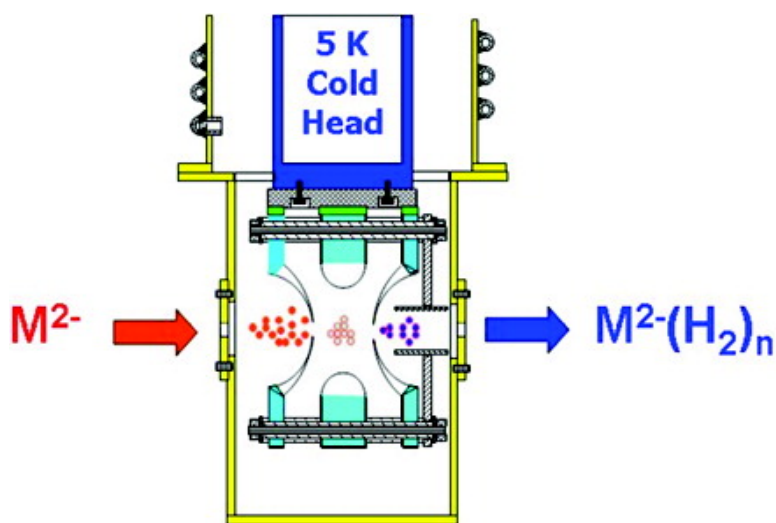


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J. Phys. Chem. A, **2008**, 112 (51), 13271-13274 • DOI: 10.1021/jp808769m • Publication Date (Web): 13 November 2008

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Observation of H₂ Aggregation onto a Doubly Charged Anion in a Temperature-Controlled Ion Trap

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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 H₂ aggregation onto a doubly charged anion, ⁻O₂C(CH₂)₁₂CO₂⁻ (DC²⁻). Weakly bound DC²⁻(H₂)_n clusters were formed in a temperature-controlled ion trap and studied using photoelectron spectroscopy. The onset of clustering was observed at 30 K, whereas extensive condensation was observed at 12 K with *n* up to 12. Photoelectron spectra were obtained for DC²⁻(H₂)_n (*n* = 0–6) at 193 and 266 nm. The spectra of DC²⁻(H₂)_n were observed to be identical to that of the bare DC²⁻ dianion except a slight blue shift, indicating the weak interactions between H₂ and the parent dianion. The blue shift on average amounts to ~34 meV (3.3 kJ/mol) per H₂, which represents the lower limit of the H₂ binding energy to DC²⁻.

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 H₂ 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 H₂ 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 H₂ binding affinity.^{11–14}

Studies of gas phase clusters containing H₂ can provide microscopic insight into interactions of H₂ 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 H₂ have been reported.^{15–26} However, there have been few studies about H₂ clustering on complex ions, mainly because of the difficulties to create such H₂ solvated clusters, which requires extremely cold environments. Recent advances in ion trap technology have made it possible to produce cold ions at very low temperatures^{27,28} 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⁺(H₂)_n.²⁸

Here we report observation of H₂ aggregation onto a doubly charged dicarboxylate dianion, ⁻O₂C(CH₂)₁₂CO₂⁻ (DC²⁻), in a temperature-controlled Paul trap containing a low pressure H₂ background gas. The threshold temperature for H₂ nucleation was observed to be ~30 K and extensive aggregation was observed at 12 K, forming DC²⁻(H₂)_n clusters with *n* up to 12. Photoelectron spectra of DC²⁻(H₂)_n (*n* = 1–6) display identical spectral features to that of the parent DC²⁻ with only a very slight increase of the electron binding energies with *n* (on average of ~34 meV per H₂ 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,^{8–10} the current work may be pertinent to understanding the intermolecular interactions of H₂ in these promising hydrogen-storage materials.

Experimental Methods

The experiment was performed with a low-temperature apparatus, which couples an electrospray ionization (ESI) source and a temperature-controlled Paul trap with a magnetic-bottle photoelectron analyzer. Details of this apparatus have been recently published³³ and only a brief account is given here. The DC²⁻ anions were produced using ESI from a 1 mM solution, prepared by desolving the corresponding acid in water along with NaOH and then diluting the neutralized solution by methanol to achieve a methanol/water ratio of 3/1. Anions from the ESI source were guided by a RF-only quadrupole into a quadrupole mass filter operated in the RF-only mode. Following the mass filter, the anions were directed into the temperature-controlled Paul trap via a 90° ion bender and an octopole ion-guide. Ions were collisionally cooled by a 0.1–1 mTorr helium background gas containing 20% H₂ (~0.02–0.2 mTorr H₂ partial pressure) before being pulsed out at a 10 Hz repetition rate into the extraction zone of a time-of-flight (TOF) mass spectrometer. The lowest ion trap temperature achieved was 12

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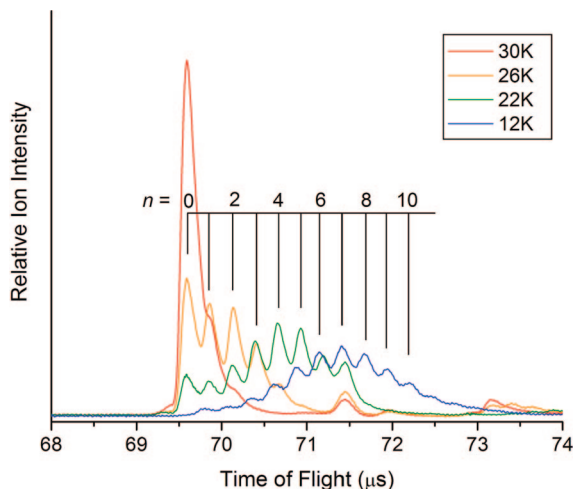


Figure 1. Temperature-dependent mass spectra of ${}^{-}\text{O}_2\text{C}(\text{CH}_2)_{12}\text{CO}_2^{-}(\text{H}_2)_n$. Note the onset of H_2 clustering at 30 K and the increasing aggregation of H_2 with decreasing temperatures. The weak peaks at 71.4 and 73.2 μs in the 30 K spectrum were due to unidentified impurities.

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 DC^{2-} 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 ClO_2^{-} . The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the respective detachment photon energies. The energy resolution ($\Delta E/E$) 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 DC^{2-} 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 DC^{2-} . This observation suggested that the H_2 molecules used as background gas for collisional cooling in the ion trap began condensing onto the cold doubly charged parent DC^{2-} to form $\text{DC}^{2-}(\text{H}_2)_n$ clusters. The onset of the H_2 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 DC^{2-} 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

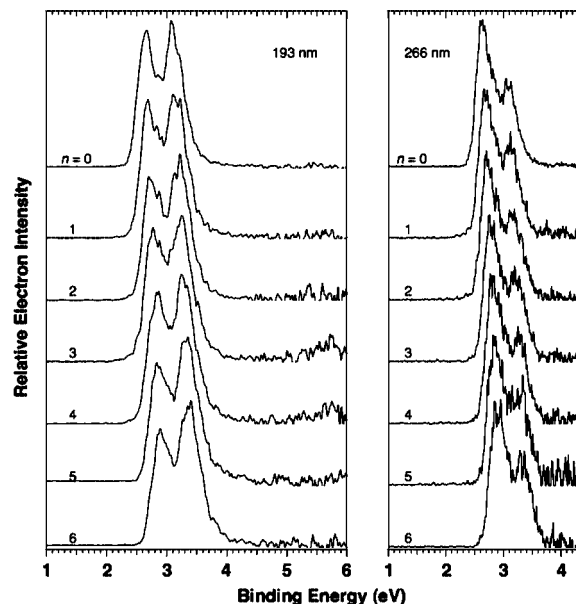


Figure 2. Low temperature photoelectron spectra of ${}^{-}\text{O}_2\text{C}(\text{CH}_2)_{12}\text{CO}_2^{-}(\text{H}_2)_n$ ($n = 0-6$) at 193 nm (left) and 266 nm (right).

TABLE 1: Adiabatic Detachment Energies (ADE) and Incremental Stabilization Energies, $\Delta\text{ADE}(n) = \text{ADE}(n) - \text{ADE}(n-1)$ of ${}^{-}\text{O}_2\text{C}(\text{CH}_2)_{12}\text{CO}_2^{-}(\text{H}_2)_n$ ($n = 0-6$)^a

n	ADE ^b	ΔADE^c
0	2.503 (10)	
1	2.515 (10)	0.012 (5)
2	2.568 (10)	0.053 (5)
3	2.616 (10)	0.048 (5)
4	2.636 (10)	0.020 (5)
5	2.675 (10)	0.039 (5)
6	2.704 (10)	0.029 (5)

^a All energies are in eV. Numbers in parentheses represent experimental uncertainties in the last digits. ^b 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 ^c ΔADE carries a smaller uncertainty because the spectral shift can be measured more accurately.

intermolecular interactions, we obtained the photoelectron spectra of $\text{DC}^{2-}(\text{H}_2)_n$ for $n = 0-6$ at 193 and 266 nm, as shown in Figure 2. We observed that the spectra of $\text{DC}^{2-}(\text{H}_2)_n$ are identical to those of the parent DC^{2-} except a small shift to higher binding energies, confirming that these newly formed species at low temperatures are indeed due to weakly bound H_2 clusters. The photoelectron spectra of DC^{2-} consist of two spectral bands due to detachment from the O lone-pair electrons from the terminal $-\text{CO}_2^{-}$ 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 H_2 molecule, defined as $\Delta\text{ADE}(n) = \text{ADE}(n) - \text{ADE}(n-1)$, is also given in Table 1. The ADE increases very slightly with the number of H_2 molecules, ranging from 0.012 to 0.053 eV, due to the very weak van der Waals or electrostatic interactions between H_2 and DC^{2-} .

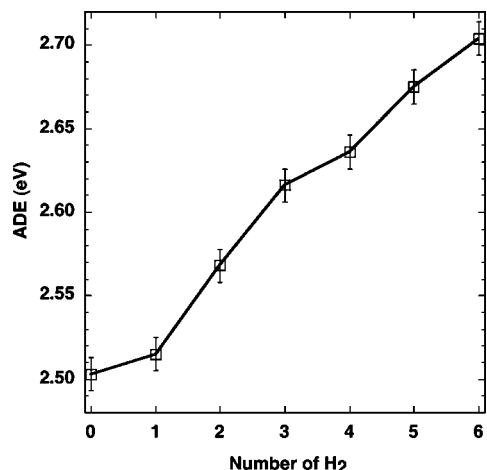


Figure 3. Adiabatic detachment energies (ADE) of $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}(\text{H}_2)_n$ ($n = 0-6$) as a function of the number of H_2 molecules.

The $\Delta\text{ADE}(n)$ 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-} . $\Delta\text{ADE}(n)$ is related to the incremental H_2 binding energies (BE) to the DC^{2-} dianion and the DC^{-} monoanion: $\Delta\text{ADE}(n) = \text{BE}[\text{DC}^{2-}(\text{H}_2)_n] - \text{BE}[\text{DC}^{-}(\text{H}_2)_n]$. Because $\text{BE}[\text{DC}^{-}(\text{H}_2)_n] > 0$, the average ΔADE 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,^{32,34–37} 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 $^{-}\text{CO}_2$ 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.^{32,34} We have investigated extensively the solvation of dicarboxylate dianions by H_2O previously and observed that water molecules solvate the two hydrophilic $^{-}\text{CO}_2$ groups alternately at both ends while avoiding the hydrophobic $-(\text{CH}_2)_n-$ backbones.^{32,35–37} A strong odd–even effect was observed in the ΔADE 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 $^{-}\text{CO}_2$ 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 $^{-}\text{CO}_2$ group. Because of the stronger electrostatic interactions, we expected that H_2 should interact with the two terminal $^{-}\text{CO}_2$ 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 two terminal $^{-}\text{CO}_2$ groups separately. We expected that the additional H_2 molecules should also bound to the $^{-}\text{CO}_2$ 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 $^{-}\text{CO}_2$ at one end. The observed trend of $\Delta\text{ADE}(n)$

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 $\text{DC}^{2-}(\text{H}_2)_n$ 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 $^{-}\text{CO}_2$ 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.

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