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On enhanced hydrogen adsorption on alkali (cesium) doped C₆₀ and effects of the quantum nature of the H₂ molecule on physisorption energies

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ABSTRACT

Hydrogen storage by physisorption in carbon based materials is hindered by low adsorption energies. In the last decade doping of carbon materials with alkali, earth alkali or other metal atoms was proposed as a means to enhance adsorption energies, and some experiments have shown promising results. We investigate the upper bounds of hydrogen storage capacities of C₆₀Cs clusters grown in ultracold helium nanodroplets by analyzing anomalies in the ion abundance that indicate shell closure of hydrogen adsorption shells. On bare C₆₀⁺, a commensurate phase with 32H₂ molecules was identified in previous experiments. Doping C₆₀ with a single cesium atom leads to an increase in relative ion abundance for the first 10H₂ molecules, and the closure of the commensurate phase is shifted from 32 to 42H₂ molecules. Density functional theory calculations indicate that thirteen energetically enhanced adsorption sites exist, where six of them fill the groove between Cs and C₆₀ and 7 are located at the cesium atom. We emphasize the large effect of the quantum nature of the hydrogen molecule on the adsorption energies, i.e. the adsorption energies are decreased by around 50% for (H₂)C₆₀Cs and up to 80% for (H₂)C₆₀ by harmonic zero-point corrections, which represent an upper bound to corrections for dissociation energies (D_e to D₀) by the vibrational ground states. Five normal modes of libration and vibration of H₂ physisorbed on the substrate contribute primarily to this large decrease in adsorption energies. A similar effect can be found for H₂ physisorbed on benzene and is expected to be found for any other weakly H₂-binding substrate.

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Introduction

Adsorption on nanotubes, fullerenes and other porous carbonaceous materials shows promise for high-density storage of H_2 and other hydrogen-rich molecules [1–9] and may be an alternative to other hydrogen-storage technologies [10–16]. However, potential well depths for physisorption are shallow (about 50 meV per H_2 molecule for adsorption on bare C_{60}) while chemisorption energies are high (about 2.1 eV per H atom for fullerenes, H_nC_{60}) [17]; these values are not compatible with the goal of high storage capacity and efficient, reversible hydrogen release at ordinary temperatures. Doping with alkali or earth alkaline metals promises to elevate adsorption energies and storage capacities to 5 wt % or more [18–21]. Doping also stabilizes the substrates against destruction during the ad/desorption process [22,23]. For alkalis the main mechanism for the increase in physisorption energy is charge transfer from the adsorbate to the degenerate lowest unoccupied molecular orbital of C_{60} .

In 2006 Sun et al., using DFT, predicted an astounding hydrogen storage capacity of lithium doped C_{60} [24]. The icosahedral $C_{60}Li_{12}$ was predicted to physisorb 5 H_2 molecules per Li which would be equivalent to a hydrogen storage capacity of 13.1 wt %. The hydrogen molecules are bound to $C_{60}(Li)_{12}$ with an average binding energy (D_e) of 0.075 eV per H_2 . A bare neutral lithium atom only binds a single H atom with 2.49 eV, whereas a Li cation binds 6 H_2 molecules. A binding energy of 0.253 eV was reported for H_2-Li^+ [24]. Two years later in 2008 Chandrakumar and Gosh calculated H_2 adsorption on C_{60} doped with Li, Na or K atoms [20]. They reported that up to six H_2 molecules bind to each adsorbed Na; the adsorption energies are enhanced relative to H_2 adsorption on bare C_{60} due to the polarization interaction with the adsorbed alkali cations. For comparison, eight H_2 can be adsorbed with approximately equal adsorption energies on a free Na^+ ion; the presence of C_{60} blocks two of those eight sites. Since then many theoretical studies have been published on hydrogen adsorption on carbonaceous materials doped with alkali, earth alkali, and other metals [25–29].

A more complex behavior has been reported for adsorption of atomic hydrogen at $C_{60}Li_6$ by Wang and Jena [18]. The lowest energy configuration consists of 5 exohedral Li and one endohedral Li; each exohedral Li physisorbs one H_2 molecule. The remaining hydrogen is chemisorbed at the 30 carbon atoms that are not linked to the exohedral Li. Such a complex, $H_4C_{60}Li_6$, would have a gravimetric hydrogen storage density of 5 wt %. Experiments performed on bulk samples of lithium- and sodium intercalated C_{60} have proven enhanced values for hydrogen uptake compared to pure C_{60} . As much as 5 wt % of H_2 could be reversibly chemisorbed and desorbed in $C_{60}Li_6$ and $C_{60}Li_{12}$; the storage capacity of $C_{60}Na_6$ and $C_{60}Na_{10}$ was found to be slightly lower [22,30–33]. Moreover, the temperature of the onset of desorption was reduced to about 250–300 °C, well below the temperature (>500 °C) at which hydrogen starts to desorb from pure fullerenes [33,34]. Optical spectroscopy, X-ray diffraction, neutron diffraction, NMR and Muon Spin Relaxation have been applied to probe the dynamics and structural changes that accompany ad- and desorption of hydrogen [23,30–33,35–39]. Laser-desorption mass spectra of

hydrogenated alkali-doped C_{60} solids show evidence for the presence of H_nC_{60} (n up to 48) fullerenes [23]; other spectra show $H_nC_{60}^+$ ions containing as many as 60 hydrogen atoms [32]. Curiously, though, no trace of H_nC_{60} -alkali ions was reported [23,32].

The present work was stimulated by those reports but here we take an alternative, bottom-up approach. Helium nanodroplets are formed in a supersonic jet and successively doped with C_{60} , cesium and H_2 . Mass spectra of these complexes reveal ions that are particularly stable. For practical purposes we used cesium rather than lithium or sodium because the large mass of cesium avoids any ambiguity when analyzing the composition of the ions.

In particular, we study hydrogen adsorption on C_{60} -cesium complexes experimentally and theoretically to address the following questions: i) Does cesium enhance hydrogen uptake in the same way that lighter alkalis do? ii) How many hydrogen atoms exhibit enhanced binding to $C_{60}Cs^+$? iii) What is the effect of a single adsorbed cesium atom on the number of hydrogen atoms in a complete solvation shell surrounding C_{60}^+ ? The experimental data suggest that up to 10 H_2 molecules experience enhanced adsorption on $C_{60}Cs^+$ compared to pristine C_{60}^+ .

Accompanying density functional calculations including dispersion interactions elucidate structure and energetics of the clusters. Adsorption energies are strongly affected by the quantum nature of the light nuclei of H_2 . Energies decrease significantly upon inclusion of harmonic corrections for the vibrational ground state energies in the complex and its constituents in all degrees of freedom. An estimate for anharmonic effects is given for the radial mode; these also play a notable role for hydrogen adsorption energies. However, more accurate predictions of the vibrational spectrum on a highly accurate multidimensional (at least 5 dimensions) potential energy surface of $(H_2)C_{60}^{0,+}$ would be needed. A Rigid Body Diffusion Quantum Monte Carlo calculation on a fitted model potential revealed a similarly large effect of vibrational zero-point corrections for H_2 physisorbed on benzene [40]. The comparison with the benzene model system shows that dispersion corrected density functional calculations with $\omega B97X-D$ including harmonic zero-point corrections and the moderate basis set LANL2DZ can provide a qualitative picture for H_2 adsorption energies on C_{60} , with slightly overestimated zero-point energies (ZPE).

Experimental results

Sections of a mass spectrum of helium nanodroplets doped with C_{60} , Cs, and H_2 are displayed in Fig. 1. $H_nC_{60}^+$ ions ($n = \text{integer}$) appear in the upper panel; these ions have been studied before [17,41]. Cesiumnated $H_nC_{60}Cs^+$ ions are seen in the lower panel. Some mass peaks are labeled. However, the presence of isotopologues needs to be taken into account when interpreting the spectrum. For example, the $H_{20}C_{60}Cs^+$ mass peak contains significant contributions from $H_{19}^{13}C^{12}C_{59}Cs^+$, $H_{18}^{13}C_2^{12}C_{58}Cs^+$ etc., plus a water impurity that is not fully resolved.

Figs. 2 and 3 display the abundance of ions extracted from the mass spectrum (Fig. 1), corrected for the occurrence of

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