

Vibrational properties of TiH_n complexes adsorbed on carbon nanostructures

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Received 11 April 2007; in final form 25 June 2007

Available online 1 July 2007

Abstract

According to recent theoretical studies, carbon nanostructures decorated with light transition metals could provide a route towards room temperature reversible hydrogen storage, a major roadblock for fuel-cell powered vehicles. Vibrational spectroscopies are the ideal experimental techniques to confirm the recent predictions of a metal–hydrogen bond of about 0.5 eV per H_2 molecule, which is expected to enable H_2 desorption at moderate temperatures. Here, we report first-principles results of the vibrational spectrum of representative systems, namely, TiH_n complexes adsorbed on fullerenes. The obtained distinctive features should be found in a successful experimental realization of these materials.

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1. Introduction

The problem of storing hydrogen is one of the most important bottlenecks for the development and application of fuel-cell technologies. It is necessary to identify a storage medium that complies with volumetric and gravimetric requirements and, in addition, presents good kinetics of hydrogen-absorption (e.g. for on-board refilling in automotive applications) and desorption. In particular, desorption at sufficiently high rates should occur at moderate temperatures (of about 100 °C), so that the required heating can be provided, for example, by a working car engine directly.

The vast majority of research on hydrogen storage, attempts to achieve practical goals based on the classical gas–solid interactions of physisorption (as in high surface area materials) or on chemisorption (as is essentially the

case of complex metal hydrides). However, storage media based on physisorption are not effective in retaining the hydrogen at room temperature, and alternatives based on chemisorption require high desorption temperatures of several hundreds of degrees Celsius. On the other hand, recent theoretical studies [1–3] suggest that nanostructure-supported light transition metals constitute ideal binding sites for H_2 molecules. So far, the best studied case is that of Ti adsorbed on nanotubes [1] or fullerenes [2,3], for which first-principles calculations predict that each Ti atom can bind up to four hydrogen molecules with a binding energy of about 0.5 eV per H_2 . Remarkably, the magnitude of the interaction lies midway between physisorption and chemisorption, which should result in hydrogen desorption at ambient conditions (that is, near room temperature and at 1 atm H_2 pressure), exactly as required. The calculations have also shown that the Ti– H_2 binding mechanism fits very well what is known in Organometallic Chemistry as a ‘Kubas interaction’ [1,4], which involves a donation of charge from the highest occupied orbital of the H_2 molecule to the metal empty states and a subsequent back donation from filled d states to the lowest unoccupied orbital of the hydrogen molecule.

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The publication of Refs. [1–3] generated considerable interest [5–7], and attempts are being made to synthesize transition metal coated carbons with the predicted high-capacity hydrogen storage properties. In our opinion, the main focus at this point should be on the experimental demonstration of the predicted Kubas-like metal–hydrogen interaction with a binding energy per molecule of about 0.5 eV. Vibrational spectroscopies are the ideal tool to characterize interactions at the atomic scale. Thus, in order to provide reference results to compare experiments with, we have performed a first-principles study of the vibrational properties of various TiH_n complexes adsorbed on C_{60} , which are representative systems. We find that the peculiar metal–hydrogen interaction leads to distinctive features in the vibrational spectrum, which presents twisting and stretching modes at frequencies significantly different from those typical of titanium hydride or hydrogen molecules, respectively.

2. Technical details

We used the generalized gradient approximation [8] to density functional theory (DFT) [9,10] as implemented in the code VASP [11]. We used the PAW scheme [12,13] to represent the atomic cores, and fully considered the following electrons: 2s and 2p of C; 3s, 3p, 3d, and 4s of Ti; and 1s of H. We used a 16 Å-side cubic supercell and a 400 eV plane-wave cut-off. We checked our calculation conditions lead to sufficiently converged results. Spin polarization was considered only in the calculations of the C_{60}Ti complex, which, as shown by previous work [3], is the only magnetic system considered here.

Fig. 1 shows the model systems studied and the data in Table 1 characterizes the first-principles relaxed structures. We considered Ti adsorbed on a C=C double bond, which we had previously identified as the most stable adsorption site [3]. (We also considered other adsorption sites, e.g. carbon hexagons and pentagons, and obtained results that do not differ significantly from those reported here.) The considered TiH_n complexes had also been previously identified as the most stable configurations for the various hydrogen loadings [3]. Total energy calculations predict $\text{C}_{60}\text{TiH}_2-3\text{H}_2$ and $\text{C}_{60}\text{Ti}-4\text{H}_2$ to be nearly-degenerate in energy and, thus, we considered both of them in this study. Note that one Ti atom takes a maximum of four H_2 molecules, a fact that has been recently discussed from the perspective of the so-called 18-electron rule [5]. The electron transfers from Ti to the C_{60} and H_2 molecules can be computed and were already published in Ref. [3]. Very briefly, let us recall that the Ti donates about one electron in its binding to the C_{60} , and a total of 1.2–1.3 electrons to the surrounding hydrogens. More precisely, in the case of $\text{C}_{60}\text{Ti}-4\text{H}_2$, approximately 0.3 electrons are transferred to each hydrogen molecule; in the $\text{C}_{60}\text{TiH}_2-3\text{H}_2$ case, the dissociated H_2 molecule takes a total of 0.6 electrons, each of the azimuthal molecules receives about 0.2 electrons, and the apical H_2 takes about 0.3 electrons. Thus, the calcula-

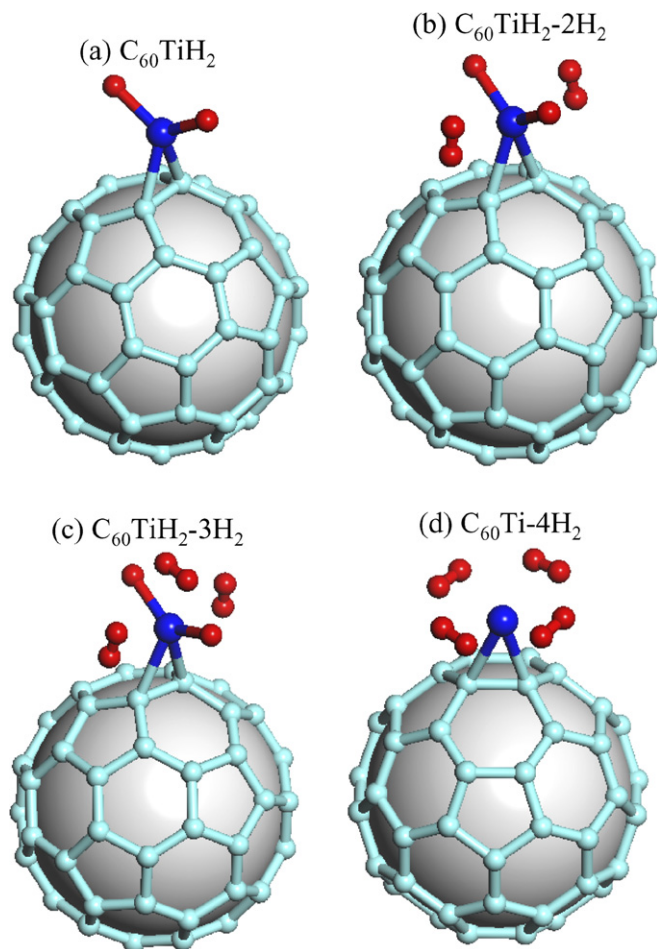


Fig. 1. Optimized structures of the four TiH_n complexes on C_{60} considered in this study.

Table 1

Relevant structural parameters, obtained from first-principles, for the $\text{C}_{60}\text{TiH}_n$ systems of Fig. 1

$\text{C}_{60}\text{TiH}_2$	Ti–H: 1.73; H–H: 2.96; Ti–C: 2.07; C–C: 1.55; H–Ti–H: 118.1
$\text{C}_{60}\text{TiH}_2-2\text{H}_2$	Ti–H: 1.73; H–H (atomic H's): 2.91; H–H (intramolecular): 0.79; Ti–C: 2.16; C–C: 1.50; H–Ti–H: 114.7
$\text{C}_{60}\text{TiH}_2-3\text{H}_2$	Ti–H: 1.73; Ti–C: 2.19; C–C: 1.49; H–Ti–H: 129.3; H–H (intramolecular apical): 0.85; H–H (azimuthal, intra and intermolecular): 0.79, 1.73
$\text{C}_{60}\text{Ti}-4\text{H}_2$	Ti–H: 1.85–1.92; Ti–C: 2.15, 2.24; C–C: 1.51; H–H (intramolecular): 0.85–0.86; H–H (intermolecular): 1.69, 1.84, 1.90

Distances are given in Angstroms and angles in degrees. Minimum and maximum values are given in cases in which there is significant dispersion.

tions indicate that the Ti atoms in the considered complexes are in a valence state of approximately +2.2.

We also performed calculations for a few reference systems, namely, C_{60}Ti , TiH_2 and the H_2 molecule. In particular, for TiH_2 we performed both the calculations and neutron spectroscopic measurements (see below), so as to

establish the accuracy of our DFT methods. For all the systems considered, we calculated the full vibrational spectrum, although we limit our discussion to the modes that involve the TiH_n complexes. We used a finite-displacement scheme for the calculation of the vibrational spectrum, employing a $2 \times 2 \times 2$ supercell to obtain approximate phonon dispersion in the case of TiH_2 . The inelastic neutron scattering (INS) spectrum was computed in the standard way [14,15].

Neutron vibrational spectroscopy measurements were performed at the NIST Center for Neutron Research. The spectrum was collected for a TiH_2 powder sample at a temperature of 4 K, using the filter analyzer neutron spectrometer [16] under conditions that provided full-width-at-half-maximum energy resolutions of 2–4.5% of the incident energy over the range probed.

3. Results

Fig. 2 shows the calculated vibrational density of states of the systems considered as would be obtained from inelastic neutron scattering. Hydrogen scatters neutrons much more effectively than C and Ti; hence, the spectral features in Fig. 2 correspond mostly to the hydrogen-dominated modes we are interested in. The top-right inset shows the experimental and calculated results for TiH_2 , focusing on the frequency range where the hydrogen modes lie. Note the characteristic good agreement between experiment and theory, as the calculations reproduce even subtle features as the two-phonon tail at high frequencies. Such is the level of agreement that should be expected for our $\text{C}_{60}\text{TiH}_n$ systems.

Table 2 gives the frequencies, and frequency ranges, in which we find the various types of modes. Representative modes are marked in the table and sketched in Fig. 3.

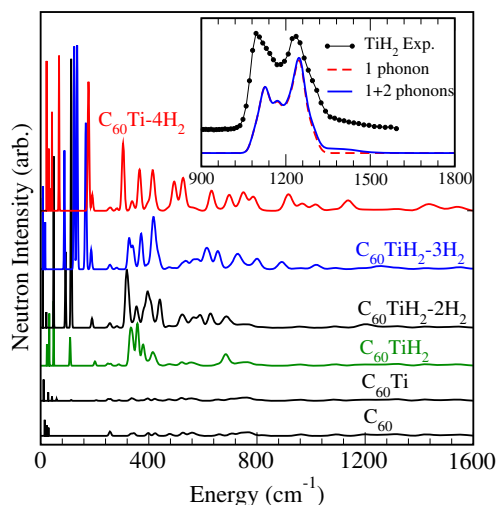


Fig. 2. Calculated vibrational density of states of the various $\text{C}_{60}\text{TiH}_n$ systems considered. The intensities are calculated so as to reproduce the results of an inelastic neutron scattering experiment. Thus, only modes dominated by hydrogen contribute significantly to the spectrum. The top-right inset shows experimental and theoretical results for TiH_2 .

Table 2

Characteristic mode frequencies (in cm^{-1}) for the various TiH_n complexes are considered

TiH_n complex	Ti	TiH_2	$\text{TiH}_2\text{-}2\text{H}_2$	$\text{TiH}_2\text{-}3\text{H}_2$	$\text{Ti-}4\text{H}_2$
Tang. \perp C=C	59	48	48	44	68
Tang. \parallel C=C	113	108	92	88	42
Radial	206	201	190	187	191
Twists/librons	–	330–700	257–600	124–1020	305–632
Ti–H stretch	–	1670/1683	1658/1670	1635/1649	–
Ti– H_2 stretch	–	–	630–744	1245/1275	678–1459
				az.	
	–	–	1188– 1218 def.	1553 ap.	1536–1553 def.
Mixed modes	–	–	–	687–1020	–
H–H stretch	–	–	3682/3700	2858 ap.	2623–2845
	–	–	–	3591/3610	–
				az.	

The abbreviations ‘ap.’, ‘az.’, and ‘def.’ stand for ‘apical’, ‘azimuthal’, and ‘deformed’, respectively. Ti– H_2 stretching modes denoted as ‘def.’ involve significant deformation of the H_2 molecule. Frequency pairs separated by a slash are given for couples of related modes corresponding to in-phase and out-of-phase atomic movements. Animations of these modes can be obtained from the authors.

4. Discussion

The discussion of our results is quite straightforward. Let us start by noting the most distinctive features obtained.

In the cases in which molecular hydrogen is present, the H–H bond-stretching mode has frequencies ranging from about 2850 cm^{-1} (for the apical H_2 molecule of $\text{C}_{60}\text{TiH}_2\text{-}3\text{H}_2$) to about 3700 cm^{-1} (e.g. in the $\text{C}_{60}\text{TiH}_2\text{-}2\text{H}_2$ case). Such frequencies are significantly smaller than what would be obtained for weakly interacting (e.g. physisorbed) H_2 molecules, i.e. around 4400 cm^{-1} as for isolated H_2 [17]. The origin of this softening can be easily deduced from the discussion in [1]: The Kubas-bonded H_2 molecule drags some charge (about 0.3 electrons) from the Ti atom and, thus, its anti-bonding state gets populated. This effect results in a weakened H–H bond and, accordingly, a lower stretching mode frequency. It should be possible to detect such low-lying H_2 stretching modes using, for example, Raman spectroscopy.

A second distinctive feature pertains the Ti–H modes involving atomic hydrogen. Such bonds are predominantly ionic, the charge transfer from Ti to H being of about 0.3 electrons per hydrogen. (As discussed in Ref. [1], H_2 molecules dissociate when the charge transfer from the Ti approaches 0.3 electrons per hydrogen [4].) The calculated frequencies are, in all the cases considered, of about 1650 cm^{-1} , i.e. they lie in a range that is well separated from typical Ti–H stretching mode frequencies in titanium hydride TiH_2 (see Fig. 2). This result suggests that the Ti–H stretching modes can be taken as a fingerprint of the TiH_n complexes that contain atomic hydrogen.

Our calculated spectra display other features that is worth discussing. Interestingly, at low frequencies we

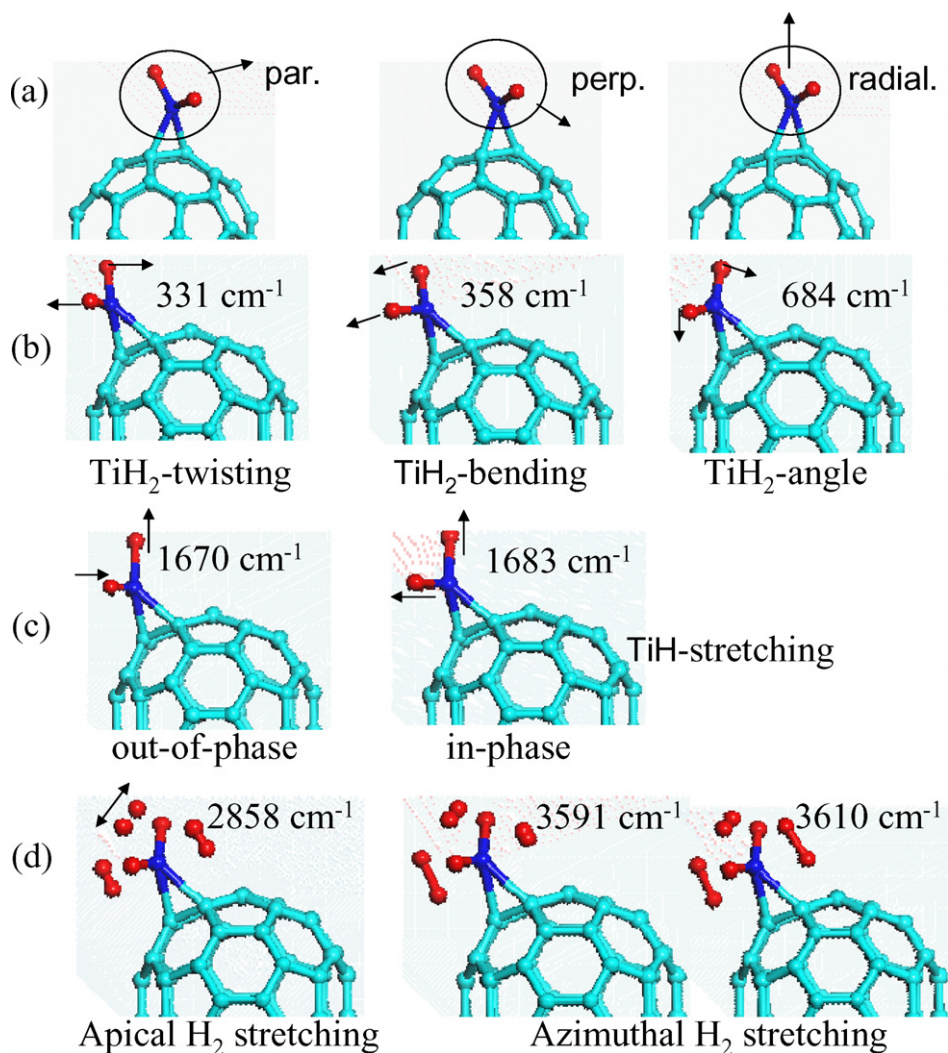


Fig. 3. Sketches of the eigenvectors of some of the modes discussed in Table 2. Panel (a) shows the vibration of the TiH₂ group parallel and perpendicular to the C–C bond as well as the radial mode. Panel (b) shows the twisting, bending, and angle-stretching modes of the TiH₂ group. Panel (c) shows the out-of-phase and in-phase TiH stretching modes, respectively. Finally, panel (d) shows the H₂ stretching modes for the top and side H₂ molecules, respectively. Animations of these and other modes can be obtained from the authors.

obtain three modes that are essentially identical for all but one of the TiH_{*n*} complexes considered (see Fig. 3a). Such modes involve the quasi-rigid displacement of the TiH_{*n*} complex and are thus directly related to the binding of the Ti atom to the fullerene. More specifically, as shown in Table 2, we have a radial mode at about 200 cm⁻¹ as well as two tangential modes, longitudinal and transversal to the C=C double bond, with typical frequencies around 100 cm⁻¹ and 50 cm⁻¹, respectively. Interestingly, in the case of C₆₀Ti-4H₂, we find that the tangential modes are ordered differently, the longitudinal one being softer (42 cm⁻¹) than the transversal one (68 cm⁻¹). That C₆₀Ti-4H₂ is a particular case is not entirely surprising, as for this complex we find the H₂ molecules lying right on top of the C atoms neighboring the C=C double bond (see Fig. 1), which clearly indicates significant H–C interactions.

The bands of twisting modes (i.e. librations) also present interesting features. Most remarkably, we do not observe

very low-energy modes associated with hindered rotations of the H₂ molecules; instead, we find very well-defined librational modes of the H₂ molecule with energies around 200 cm⁻¹ and above. This suggests that, because the interactions are relatively strong, the rotational angular momentum is not a good quantum number for H₂ molecules bonded to Ti atoms, and one should not expect to observe quantum-mechanical effects associated to *ortho-para* transitions.

Groups of related twisting modes can be readily identified. In all of them, the highest modes are essentially pure hydrogen modes, whereas the lowest ones include significant contributions from carbon atoms. Of course, such an effect is mainly caused by the mass difference between C and H, but it also reflects significant H–C interactions. In the case of C₆₀TiH₂-3H₂, the twisting modes cover a remarkably wide frequency range, extending approximately from 120 cm⁻¹ to 1000 cm⁻¹. We find that this dispersion, which appears to be quite large as compared with

that obtained for $C_{60}Ti-4H_2$, is related to strong H_2-H_2 and H_2-H (atomic) interactions that in some cases cause significant mixture with $Ti-H_2$ and $Ti-H$ stretching modes. For example, we observe that modes involving displacement of the atomic hydrogens along the radial direction always come in couples: there is a hard mode in which the apical H_2 approaches the atomic hydrogen(s), and a soft mode in which it escapes from them. (Note that the movement of the apical H_2 involves $Ti-H_2$ stretching.) The soft–hard splitting in this example is of about 200 cm^{-1} , reflecting very strong interactions between the different hydrogens.

Purely stretching modes can also display soft–hard mode splittings that allow to quantify, in simple cases, the interactions between different hydrogen atoms or molecules. For example, in the case of the $Ti-H$ stretching mode of $C_{60}TiH_2$, the two frequencies given correspond to in-phase (1670 cm^{-1}) and out-of-phase (1683 cm^{-1}) displacements of the two H atoms, where by ‘out-of-phase’ we refer to the case in which the two hydrogens approach the Ti simultaneously (see Fig. 3c).

Finally, the vibrational information also reveals how the magnitude of H–H intramolecular interactions is related with that of the corresponding $Ti-H_2$ bond. The results for $C_{60}TiH_2-3H_2$ provide a very clear example of such a relationship. The characteristic $Ti-H_2$ stretching frequency is about 1260 cm^{-1} for azimuthal H_2 molecules and 1553 cm^{-1} for the apical one. On the other hand, the intramolecular stretching mode of the azimuthal H_2 (3600 cm^{-1}) is significantly higher than that of the apical molecule (2858 cm^{-1}) (see Fig. 3d), reflecting a tighter bond. The explanation for these results is straightforward: a stronger $Ti-H_2$ ionic bond implies a larger charge transfer from the titanium to the hydrogens, which results in a more populated H_2 anti-bonding orbital and, thus, a softer H–H stretching mode.

5. Summary

We have used accurate first-principles methods to compute the vibrational spectrum of various representative TiH_n complexes adsorbed on C_{60} . Our results display a number of very distinctive features directly related with the peculiar metal–hydrogen interaction that makes these systems appealing for hydrogen storage. Most remarkably, we have found anomalous H–H intramolecular stretching frequencies that can be up to 1500 cm^{-1} smaller than what is typical for isolated or physisorbed H_2 molecules. The $Ti-H_2$ and $Ti-H$ stretching modes are also shown to have distinctive frequencies, and characteristic low-energy modes involving displacements of the TiH_n complex as a whole are obtained. We have checked that our results do not depend strongly on the Ti binding site. Thus, while obtained for TiH_n groups adsorbed on fullerenes, we are

confident our conclusions remain qualitatively valid for other carbon nanostructures. The calculated features should be found, using Raman or neutron spectroscopies, in a successful experimental realization of these systems.

In conclusion, we hope our work will stimulate further attempts at experimentally confirming the theoretical predictions of such an unconventional metal–hydrogen interaction and its potential for hydrogen storage. In particular, we should note that there is already a large number of experimental studies of various organometallic complexes, including $Ti-C_{60}$ [18], which are produced by laser vaporization of the metal and then studied by time-of-flight mass and infrared spectroscopic techniques in gas phase. The extension of those studies to the hydrogen-absorption properties of such metal–molecule complexes could be a first step towards the experimental demonstration of the unique metal–hydrogen interaction discussed here.

Acknowledgements

J.I. thanks financial support from the Spanish Ministry of Science and Education, through the ‘Ramón y Cajal’ program and Grant FIS2006-12117-C04-01, and the Catalan Government Grant SGR-2005-683. T.Y. and W.Z. acknowledge partial support from DOE under BES Grant DE-FG02-98ER45701 and EERE Grant DE-FC36-04GO14282. The facilities provided by the Barcelona Supercomputing Center were used.

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