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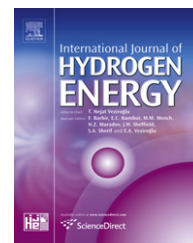
Vibrational spectra of Ti:C_2H_4(nH_2) and Ti:C_2H_4(nD_2) ($n = 1-5$) complexes and the equilibrium isotope effect: Calculations and experiment

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ABSTRACT

Calculations of the ability of titanium–ethylene complexes of the type, Ti:C_2H_4, to absorb molecular hydrogen have been performed using density functional theory. A maximum of 5H_2 molecules can be adsorbed on Ti:C_2H_4 thereby giving an uptake capacity of 11.72 wt%, in excellent agreement with previous experimental results reported by two of us (Phys. Rev. Lett., 100, 105505, 2008). Calculations of the vibrational frequencies in such complexes with both H_2 and D_2, Ti:C_2H_4(nH_2) and Ti:C_2H_4(nD_2), $n = 1-5$, have also been performed and the values obtained used to find the Equilibrium Isotope Effect (EIE). Measurements of the EIE are also reported and these are in excellent agreement with the EIE calculated for 5H_2 molecules adsorbed in the complex.

1. Introduction

An outstanding problem for the realization of hydrogen as a transportation fuel is the lack of safe and economical ways to store hydrogen on board. Hence discovery of new materials that can store hydrogen with high gravimetric and volumetric density, and that exhibit fast hydrogen sorption and desorption kinetics under ambient thermodynamic conditions are essential for practical applications. In this context, different carbon based nanostructures such as carbon nanotubes [1–9], fibers [10–12], graphite [13], graphane [14] and organometallic compounds [1,5,15–25] have been suggested for storing hydrogen. Of these Ti-decorated organic

compounds in particular have been shown to be the most promising with hydrogen storage levels exceeding those found in most materials currently being evaluated for practical applications [16–19,22,23]. Recent gravimetric measurements on nanoscale clusters and thin films suggest that it is possible to store hydrogen in Ti:C_2H_4 organometallic compounds with high hydrogen uptake capacity of 12 wt%. A maximum of 5H_2 molecules are adsorbed on Ti:C_2H_4 compound experimentally [23]. However, this experimental work fell short by being unable to demonstrate desorption of the H_2 due to experimental constraints of heating the quartz sensor utilized for the nano-gravimetric measurements. An alternate method to explore the ease of removal of H_2 is to
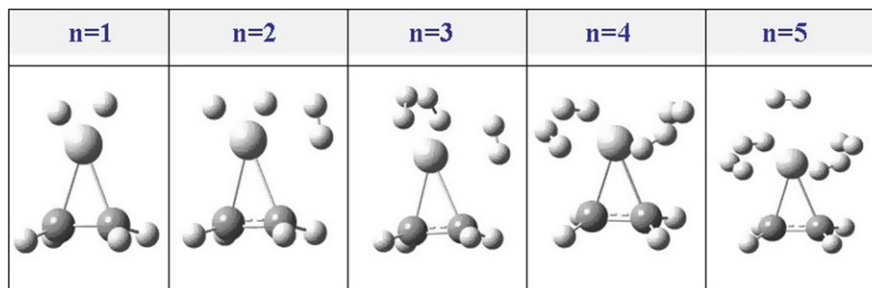
Fig. 1 — Optimized geometries of Ti:C_2H_4(nH_2) or Ti:C_2H_4(nD_2) (n = 1—5) at B3LYP/DGDZVP level of theory.

perform isotope exchange experiments, for instance with deuterium.

Both the kinetic and equilibrium isotope effects are well studied both theoretically and experimentally [26]. Theoretically the equilibrium isotope effect was first calculated by Bigeleisen and Mayer [27]. Using the notation of Wolfsberg and Stem [28], the equilibrium isotope effect is expressed as the product of three terms:

$$EIE = MMI \times EXE \times ZPE \qquad (1)$$

The MMI factor accounts for molecular masses and moments of inertia (i.e., rotational and translational partition function ratios) of the isotopic species. In most cases this factor is close to unity and is irrelevant since masses and moments of inertia do not change significantly between isotopes. However, this may not be the case when dihydrogen is involved. The second factor, EXC, arises from the presence of vibrational levels beyond the zero point level. Clearly, this factor would be important when isotopically sensitive low frequency modes are present. The third factor, ZPE, is due to the zero point energy and is usually the dominant contributor to the isotope effect. Thus a measurement of the equilibrium isotope effect and its comparison with theoretical calculations provides a good consistency check on proposed dihydrogen configurations in hydrogen storage materials.

In this article, we present calculations of the hydrogen and deuterium uptake capacity of Ti:C_2H_4 organometallic compounds and compare the results with experiments. We find that a maximum of 5H_2/D_2 molecules can be adsorbed on Ti:C_2H_4 organometallic compounds. In the case of H_2 this amounts to hydrogen uptake capacity of 11.7 wt% in excellent agreement with the experimental value of 12 wt% reported earlier [23]. We also calculate the vibration spectra of Ti:C_2H_4(nH_2) and Ti:C_2H_4(nD_2) for different n. The obtained vibrational frequencies are used to evaluate the equilibrium isotope effect (EIE), the ratio of the di-hydrogenation to the di-deuteration equilibrium rate constant. The calculated EIE of 0.66 for n = 5 is in excellent agreement with the experimental results presented here for the first time in such a complex. The average binding energy with successive addition of H_2 molecule is found to be 0.7 eV which is ideal for reversible hydrogen storage.

2. Computational and experimental details

The geometries of Ti:C_2H_4(nH_2) and Ti:C_2H_4(nD_2) (n = 1—5) are optimized using Becke's three-parameter hybrid functional combined with Lee, Yang and Parr correlation (B3LYP) functional [29] and DGDZVP basis set. The vibrational frequencies

Table 1 — Structural parameters for Ti:C_2H_4(nH_2) (n = 1—5) obtained at B3LYP/DGDZVP level. Bond lengths are in Angstrom and bond angles in degrees.

$C_2H_4TiH_2$	Ti—H: 1.74, H—H: 3.05, TiC: 2.05, C—C: 1.47 H—Ti—H: 121.9
$C_2H_4TiH_2$—H_2	Ti—H: 1.74, H—H (atomic H's): 3.03, H—H (intramolecular): 0.77, Ti—C: 2.07, C—C: 1.44 H—Ti—H: 120.6
C_2H_4Ti–3H_2	Ti—H: 1.83—1.98; H═H (near top): 0.91, 0.91; H—H (side): 0.79; Ti—C: 2.12, C—C: 1.44
C_2H_4Ti–4H_2	Ti—H: 1.95—1.96; H—H (side): 0.81, 0.81, 0.81, 0.81 Ti—C: 2.14, C—C: 1.44
C_2H_4Ti–5H_2	T—iH: 1.93—1.94; Ti-(top) H: 2.13, H—H (side): 0.81, 0.81, 0.81, 0.81; H—H (top):0.77, Ti—C: 2.20, C—C: 1.42

Table 2 — BSSE—corrected interaction energies and binding energy for Ti:C_2H_4(5H_2) complexes using B3LYP/DGDZVP level. OM represents Ti:C_2H_4 and Hi is the ith Hydrogen molecule in a complex.

Interacting molecules	Energy (kcal/mol)
OM—H1	−1.59
OM—H2	−1.59
OM—H3	−1.59
OM—H4	−1.59
OM—H5	−0.82
H1—H2	0.09
H1—H3	1.91
H1—H4	0.66
H1—H5	1.09
H2—H3	0.66
H2—H4	1.90
H2—H5	1.09
H3—H4	0.09
H3—H5	1.09
H4—H5	1.09
B.E.	−50.71