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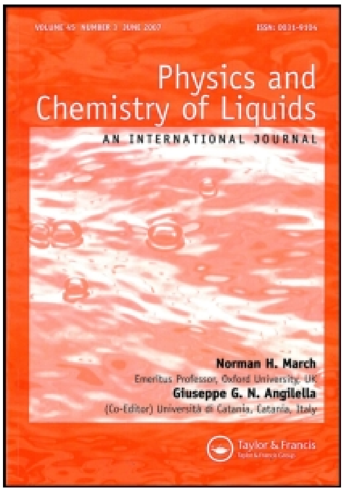

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Interaction of a hydrogen molecule with a water cage $(H_2O)_8$

I. A. Howard[a]; G. G. N. Angilella[b]; N. H. March[c]; C. Van Alsenoy[d]
[a] Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium [b] Dipartimento di Fisica e Astronomia, Università di Catania, and Lab. MATIS-INFM, UdR Catania, and INFN, Sez. Catania, Via S. Sofia, 64, I-95123 Catania, Italy [c] Donostia International Physics Center (DIPC), E-20080 San Sebastian, Spain [d] Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium

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Letter

Interaction of a hydrogen molecule with a water cage $(H_2O)_8$

I. A. HOWARD*†, G. G. N. ANGILELLA‡,
N. H. MARCH§ and C. VAN ALSENOY¶

†Department of Physics, University of Antwerp,
Groenenborgerlaan 171, B-2020 Antwerp, Belgium
‡Dipartimento di Fisica e Astronomia, Università di Catania, and Lab. MATIS-INFM,
UdR Catania, and INFN, Sez. Catania, Via S. Sofia, 64, I-95123 Catania, Italy
§Donostia International Physics Center (DIPC), E-20080 San Sebastian, Spain
¶Department of Chemistry, University of Antwerp,
Universiteitsplein 1, B-2610 Antwerp, Belgium

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We study the stability of a hydrogen molecule H_2 interacting with an octamer water cage $(H_2O)_8$, both in the D_{2d} and in the S_4 configurations. The H_2 molecule was allowed to approach the water cage along its main symmetry directions, resulting in physisorbed final configurations, with binding energy 0.01–0.06 eV, depending on the starting geometry and the level of approximation used. The vibrational spectra of all stable configurations show an increase of both IR intensity and Raman activity below $300\,\mathrm{cm}^{-1}$, due to dimer–octamer interaction. Finally, we have also considered an H_2 dimer inside a water octamer cage. In this case, we confirm a sizeable blue-shift of the H_2 frequency, as has been recently found also for the $H_2 \cdot (H_2O)_{12}$ cluster.

Keywords: Water clusters; Diatomic molecules; Octamer water cage

Dissociation of diatomic molecules by solid surfaces is a topic of considerable interest in industrial processes. More recently, because of current interests in hydrogen storage, which we return to briefly later in this Letter, the problem of a hydrogen molecule interacting with both crystalline surfaces and nanostructures has resulted in considerable activity [1–5]. A related problem is that of electron-bound water clusters – the stabilization of water clusters by the addition of an external electron [6].

Therefore, following our earlier work in this article on a free space water cluster $(H_2O)_8$ [7], we have carried out quantum chemical calculations on the interaction of a hydrogen molecule with the $(H_2O)_8$ octamer. There has been extensive discussion

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*Corresponding author. Email: iris.howard@ua.ac.be

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in the literature of the relative stability of the various possible configurations of the isolated water octamer (see, for example, [3,8]). There is general agreement that the two lowest-energy structures of the isolated octamer have D_{2d} and S_4 symmetries, with the D_{2d} structure lying marginally lower at $T=0$. Recent work by Suitte *et al.* [4] has examined the stable equilibrium positions of H_2 inside a water octamer not only for these two octamer symmetries, but for each of the 14 unique conformers of the $(H_2O)_8$ octamer; here, we focus on the interaction of H_2 with the octamer, in both the D_{2d} and S_4 configurations, primarily for the case where H_2 is initially external to the octamer. The H_2 molecule was allowed to approach the octamer along three distinct paths: (1) parallel to a cube edge, (2) parallel to a cube face with the molecular midpoint above the center of the face, and (3) with the molecular axis along the direction from the cube center to a vertex. Each possible distinct configuration was considered. Geometry optimization was carried out to determine the stable equilibrium configurations of the cluster, with all atomic positions allowed to relax. Results in the present work have been obtained with GAUSSIAN 03 at the Hartree-Fock (HF) 6-31G** level of calculation [9]; normal-mode frequency calculations were carried out to check the stability of the energetic minima found. Initial geometries of the isolated octamers were also optimized at the HF/6-31G** level. As a check of the minima found at this level of calculation, we have carried out subsequent optimizations at second-order Møller-Plesset (MP2) 6-31G** level for these configurations, beginning from the HF-determined optimal geometries, and have recalculated frequencies.

For the H_2 + octamer of D_{2d} symmetry, two distinct stable configurations were found at the HF level. In the first, the dimer lies with its axis along the direction from the cube center to a vertex. The shortest distance from a dimer H atom to the O at a cube vertex is 2.703 Å, indicating, as expected, physisorption rather than chemisorption. The octamer remains essentially undistorted; there is a decrease of just 0.01 Å in the length of a cube edge adjacent to the physisorption site. There is a very slight net (Mulliken) charge of $-0.009|e|$ on the H_2 dimer. In the second stable configuration, the H_2 sits almost perpendicular to a cube edge, above the midpoint of an H-bond; again, the geometries of both octamer and dimer are essentially unaffected, with the distance from the near end of the dimer to the nearest octamer O atom 2.991 Å, and to the nearest octamer H atom, 3.050 Å. Here, the net (Mulliken) charge on H_2 is even smaller, $-0.005|e|$. The (negative) binding energies, taken as the difference in the energy of the cluster and the sum of the energies of its isolated (geometry-optimized) components, are very small in magnitude at this level of calculation, 0.04 eV for the first configuration and only 0.01 eV for the second. The H–H distance within the dimer is unchanged, for both stable cluster configurations, from its free-space value of 0.733 Å. Subsequent MP2/6-31G** optimizations, as described above and shown in figure 1, also resulted in stable structures. For the structure with the dimer along the direction of a diagonal (see figure 1a), the nearest distance from a dimer atom to a cube vertex is decreased to 2.542 Å, with the H_2 bond length at 0.736 Å. The binding energy of the dimer to the cube is somewhat increased, to 0.06 eV; the net Mulliken charge on the dimer, calculated using the HF wavefunctions at the MP2-optimized geometry, is $-0.012|e|$. The second stable configuration, in which the dimer sits above and almost perpendicular to an H-bond (figure 1b), also shows only small refinements in distances at the MP2 level. The distance from the near end of the dimer to the nearest octamer O atom is decreased to 2.705 Å, and to the nearest octamer H atom, 2.699 Å.

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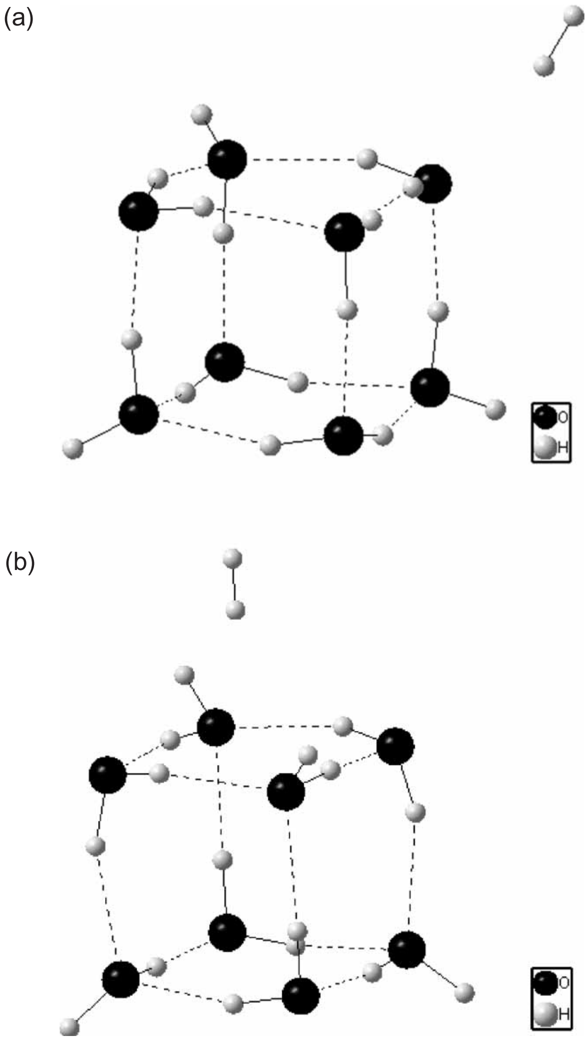

Figure 1. First (a) and second (b) stable positions, as calculated at MP2/6-31G** level, for H_2 adsorbed on the octamer of D_{2d} symmetry.

For this configuration, the MP2 binding energy is also increased from its HF value, from 0.01 eV to 0.04 eV. Net Mulliken charge on the dimer remains at $-0.005|e|$.

For the approach of H_2 to the octamer of S_4 symmetry, two stable positions were again found at the HF level. The first is analogous to the structure of figure 1(a) for the octamer of D_{2d} symmetry; again, geometries of dimer and octamer are essentially unchanged from their values in isolation. The shortest distance from a dimer H atom to the O at a cube vertex is 2.705 Å, so that physisorption is again evident. The second stable configuration is the analog of the second stable configuration of H_2 on the octamer of D_{2d} symmetry. The H-bond above which the dimer sits is elongated by just 0.01 Å; the distance from the near end of the dimer to the nearest octamer O atom is now 2.989 Å, and to the nearest octamer H atom, 3.052 Å. Binding energies are identical to those for interaction with the D_{2d} octamer, 0.04 eV for the first configuration and 0.01 eV for the second; thus, details of the octamer configuration are not important in binding at this level. Reflecting this, the net Mulliken charges on the dimer are also identical to those for the stable configurations of H_2 interacting with the D_{2d} dimer, i.e., $-0.009|e|$ for the first configuration and $-0.005|e|$ for the second. Finally, the H–H distance within the dimer again remains at its free-space value. Subsequent MP2 corrections again give results completely analogous to those for adsorption on the octamer of D_{2d} symmetry. For the first stable configuration, the binding energy increases from 0.04 eV to 0.06 eV, while for the second stable configuration, binding energy increases from 0.01 eV to 0.04 eV, while the net dimer charge is $-0.01|e|$. Structures are shown in figures 2(a) and (b).

It is informative to compare the vibrational spectra for the stable cluster configurations with those of the isolated dimer and isolated octamer. In general, the lowest

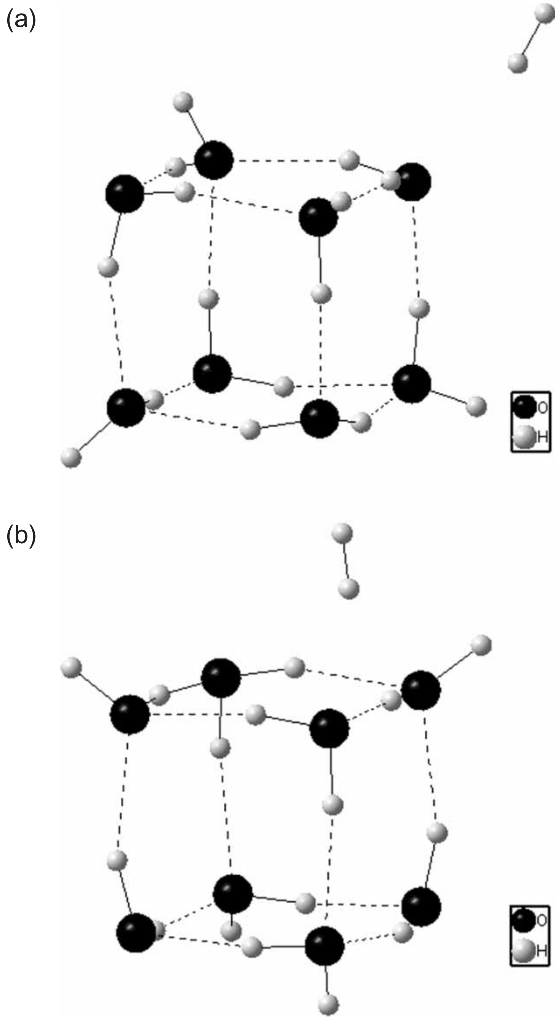

Figure 2. First (a) and second (b) stable positions, as calculated at MP2/6-31G** level, for H_2 adsorbed on the octamer of S_4 symmetry.

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couple of frequencies (below about 35 cm^{-1}) of the octamer + dimer clusters represent motion of the dimer as a whole relative to the octamer, with little relative motion of atoms within either the dimer or octamer. The highest frequency, nearly unchanged from its free-space value of 4635 cm^{-1} at HF/6-31G** level, is the stretching mode of the dimer. In figures 3(a)–(c) we show IR intensities and Raman activities for a representative vibrational spectrum calculated at the HF level (the second stable

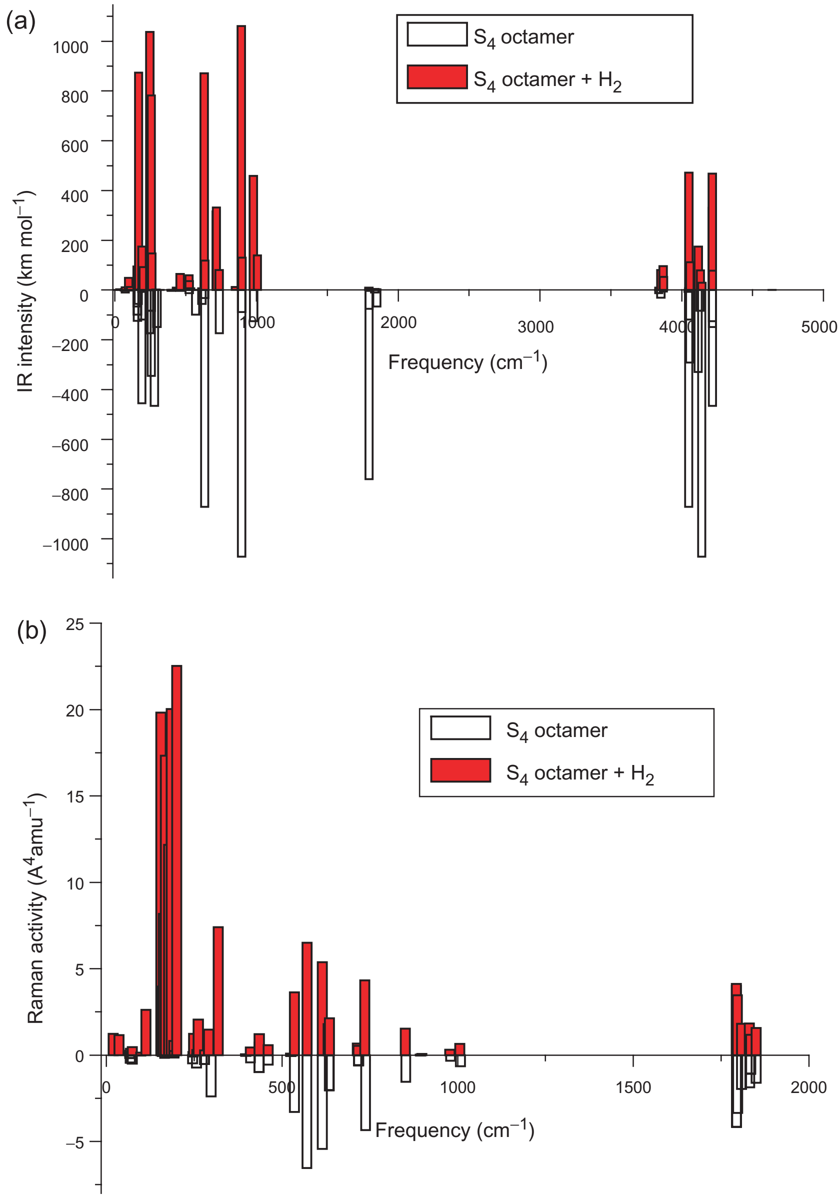

Figure 3. The IR intensity (a) and Raman activity (b) and (c) for the second stable position of the dimer on the octamer of S_4 symmetry. Intensities and activities for the isolated octamer are plotted along the negative axis for comparison.

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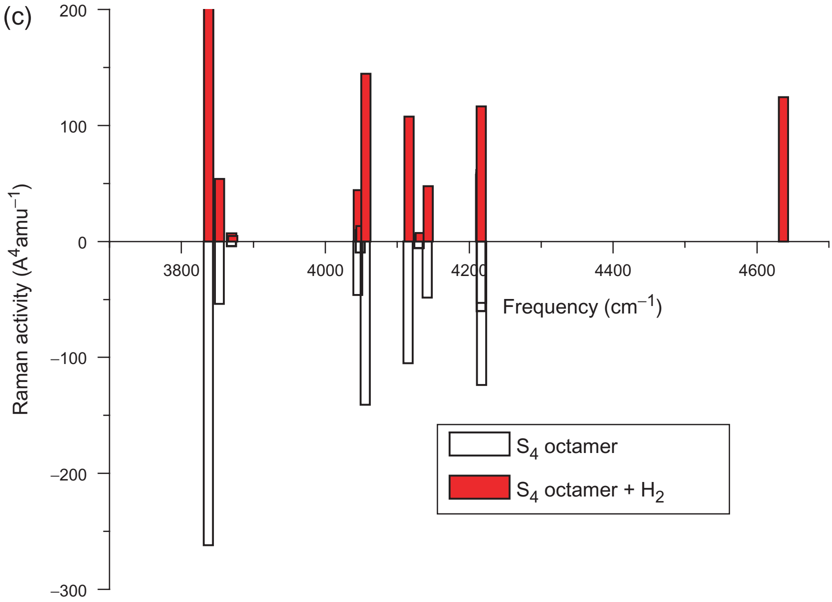

Figure 3. Continued.

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configuration described above, with the octamer of S_4 symmetry); the main features of the changes brought about by interaction are similar for all the stable structures. We compare activities for the isolated octamer with those of the dimer + octamer cluster. The IR intensities show an increase between 50 and 300 cm^{-1} due to the emergence of the low-frequency modes involving dimer–octamer interaction, and a decrease above 1500 cm^{-1}. Raman activity for similar reasons increases below 300 cm^{-1}, with a general decrease above 3800 cm^{-1}. The high-frequency dimer stretching mode is of course strongly Raman-active. At the MP2 level, the increased interaction between dimer and octamer, as demonstrated in the somewhat increased binding energies and shorter dimer–octamer bond lengths noted above, is also reflected in a frequency increase of $\lesssim 30\%$ for the modes below ≈ 1200 cm^{-1}, along with a slight increase in frequency for some of the higher-frequency modes, including the (dimer) H_2 stretch.

Finally, we have also considered a number of starting configurations in which the dimer is inside an octamer; specifically, we have considered all unique starting configurations in which the dimer lies along the line connecting centers of opposite faces of the cube, and all those in which the dimer lies along a diagonal of a plane cutting through the midpoints of edges and passing through the cube center. These configurations were considered for octamers of both D_{2d} and S_4 symmetries. Only two stable final geometries were found. For the D_{2d} octamer, a stable configuration resulted with the dimer along a line connecting centers of opposite faces of the octamer (see figure 4). This configuration is very similar to that described by Suitte *et al.* [4] for the D_{2d} cage. In this case we find a *positive* binding energy of 0.67 eV (increasing to 0.71 eV at the MP2 level), with a net Mulliken charge of $-0.038|e|$ ($-0.048|e|$ at the MP2 level) on the dimer. The dimer length decreases in this case to 0.716 Å at the MP2 level. In the vibrational spectrum, we find that the H_2 frequency is shifted

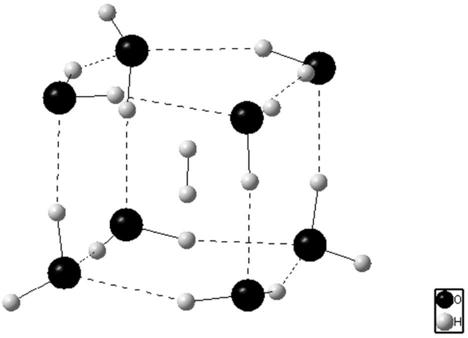

Figure 4. Stable position for the dimer inside the octamer of D_{2d} symmetry.

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from 4614 to 4855 cm^{-1}, at MP2/6-31G** level. (A general tendency towards blue-shifting in the H_2 frequency has also been confirmed in quantum chemical calculations of an H_2 molecule trapped in an $(H_2O)_{12}$ cage, where the H_2 frequency-shift turns out to be 96 to 318 cm^{-1}, depending on the method and basis used [10].) For the octamer of S_4 symmetry, an analogous starting configuration led to a quite different but also stable final configuration. For this case, as for a number of those considered by Suitte *et al.* [4], the octamer cage breaks open and the dimer escapes, disrupting three H-bonds. Subsequently, however, the cage reforms, with re-establishment of the hydrogen bonds and external bonding of the dimer to the octamer, as in the second stable configuration described above. The final distance from the near end of the dimer to the nearest octamer O atom is then 3.021 Å, and to the nearest octamer H atom, 3.213 Å. Thus escape of the dimer from the octamer cage does not necessarily mean the loss of H_2 from the system as a whole.

Suitte *et al.* [4] found positive binding energies ranging between 0.13 and 0.81 eV for H_2 in D_{2d} and S_4 structures at the MP2 level, depending on the basis set employed, with binding energies decreasing in magnitude as the basis was expanded. Our external dimer (negative) binding energies are of course considerably smaller in magnitude, on the order of room-temperature k_BT. We note that at $T=0$ the lowest-energy stable structures found in [4] were those in which the dimer was trapped inside an octamer of C_2, C_i or C_s symmetries; dimer binding energies as low as 0.07 eV for larger bases were reported for these cases.

As to further directions, as this Letter was nearing completion, we became aware of the very recent work of Maresca *et al.* [11], in which a search was made for a strong physisorption site for H_2 in Li-doped porous carbons. This work follows the extensive research conducted over the past few years on hydrogen adsorption in porous carbon solids near normal temperature and pressure conditions. Technological potential for such studies was afforded by the need to provide a suitable storage facility for transportation systems. Such motivated studies have embraced various forms of carbon, including activated microporous carbons, fibers and single-wall or multiwall C nanotubes. It is noteworthy that for single-wall nanotubes, Alonso *et al.* [12] have demonstrated that dissociative chemisorption of molecular hydrogen can be achieved. These results have been very recently confirmed by a first-principles study of Yildirim and Ciraci [13] on H_2 adsorption in titanium-decorated single-wall C nanotubes.

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