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Adsorption of H_2 on carbon-based materials: A Raman spectroscopy study

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We made use of the Raman spectroscopy to investigate the mechanism of hydrogen adsorption on carbon materials. We have recorded the Raman active roto-vibrational *Q* branch of adsorbed hydrogen at various temperatures and pressures and we have developed a qualitatively theoretical model for the interpretation of the spectra. Because of the small Raman shifts observed for the *Q* branch we conclude that no charge transfer phenomena are involved in the interaction with the adsorbing material, but only a simple physisorption takes place; moreover, no C-H stretching signals in the region of (2800–3300) were detected, thus indicating that chemisorption, if any, should be negligible.

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I. INTRODUCTION

The possible advantages which could br derived from the use of hydrogen as a new energy vector have driven an enormous interest in the scientific community, for the possible discovery of new technological developments. Behind these efforts, however, still unsolved technical problems lie and wait for a solution; among them, in the automotive field, the problem of the storage of hydrogen on board is far from being settled.[1–4]

The use of carbon-based materials (amorphous carbons, nanotubes, fullerenes, nanofibers, etc.) to store hydrogen is one of the most active fields of research, particularly because some erroneous reports (e.g., Refs. 5–7) have recently suggested that these materials could have easily solved the problem; for a comprehensive review on this topic we refer to Refs. 1 and 4.

In particular some of the large values reported for the adsorption of hydrogen,[5–7] not reproduced by other authors,[1,4] could not be explained in terms of a simple physisorption phenomenon; Dillon and Heben[8] (see also the review of Dagani)[9] suggested that an intermediate mechanism between physisorption and chemisorption, that implies charge transfer, could justify some of the results which reported supposedly large adsorptions; these astonishing results, however, were later shown to be unacceptable.[4,8,10] Many other papers[11–22] report little, or almost negligible, hydrogen adsorption in different carbon nanostructures.

Independently from the experimental errors, the research carried out was based mainly on a trial and error method. Only a few works[13,23–27] were concerned with the physics behind the behavior of these materials and tried to investigate their interactions with the hydrogen molecules.

Hydrogen could be physisorbed on carbon materials, keeping its molecular integrity, or could be chemisorbed (with the necessary dissociation of the interatomic H-H bond). In principle chemisorbed hydrogen could be detected, by means of spectroscopic methods, by analyzing the vibrations of the new C-H bonds formed, i.e., C-H out-of-plane deformation modes (IR active in the region of $700-900\ \mathrm{cm}^{-1}$)[28–31] or C-H stretching modes (IR and Raman active in the region of $2800-3300\ \mathrm{cm}^{-1}$).[28,30,31] Physisorbed hydrogen could be detected in the region near the vibration of the free molecule (Raman active $4161\ \mathrm{cm}^{-1}$).[32] If H_2 molecules would be strongly interacting with the adsorbing material, as suggested by Dillon and Heben,[8] a partial charge transfer should be expected, thus implying larger frequency shifts of the H-H stretching mode[33] ($\approx 2000\ \mathrm{cm}^{-1}/\mathrm{electron}$).

II. RAMAN SPECTROSCOPY: A TOOL FOR PROBING THE INTERMOLECULAR INTERACTIONS

Starting from the pioneering work of Rasetti,[32] numerous papers can be found in the literature that investigate the behavior of hydrogen in increasingly perturbed conditions in order to answer questions of fundamental physics and planetary science; Raman spectroscopy turns out to be one of the most useful techniques.[34–40]

When the hydrogen molecule is no longer considered as an isolated entity, the intermolecular potential perturbs the anharmonic intramolecular potential

$$\boldsymbol{V}^{\mathrm{tot}} = \boldsymbol{V}^{\mathrm{Intramolecular}}_{\mathrm{H\text{-}H}} + \boldsymbol{V}^{\mathrm{Intermolecular}}_{\mathrm{H_2(gas)\text{-}H_2(gas)}}. \tag{1}$$

The perturbation of the intramolecular potential is just the reason why molecular spectroscopy becomes a useful tool to investigate the intermolecular interactions. It was found, from experimental data,[34,35,40] that the perturbation of the Raman active *Q* branch is a function (power series) of density

$$[\upsilon_{Q(J)}]_\rho = \upsilon^0_{Q(J)} + a_J(T)\rho + b_J(T)\rho^2 + \cdots, \tag{2}$$

where ρ is the density of the gas, $\upsilon^0_{Q(J)}$ is the frequency in the limit of zero pressure (isolated molecule), a_J and b_J are constant at a given temperature. The term b_J must be considered only in the high density region. We can first express the intermolecular potential in the form of Lennard-Jones

$$\boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}(\boldsymbol{r}) = \frac{\boldsymbol{A}^{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}} - \frac{\boldsymbol{B}^{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}, \tag{3}$$

where $r_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}$ is the intermolecular distance between two interacting molecules.

From Eq. (3) it is clear that the perturbation by the isotropic intermolecular potential to the total potential [V^{tot} in Eq. (1)] is composed of two terms: one due to the repulsive forces and one due to the attractive forces.

The Raman frequency shift of the Q branch, for the pure gas,[34,35] is mainly determined by the balance of the effects of the two parts of the intermolecular potential on the stretching vibration; the attractive part has the effect of weakening the intramolecular bond and causes a downshift in frequency, the repulsive part has the effect of compressing the bond and causes an upshift in frequency

$$\Delta \boldsymbol{\upsilon}_{\text{H-H}} = \frac{\boldsymbol{K}^{\text{REP}}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}} - \frac{\boldsymbol{K}^{\text{ATT}}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(gas)-H}_2\text{(gas)}}}. \tag{4}$$

In the case of hydrogen at ambient temperature the two effects almost compensate each other.[34,35]

From the literature[34–40] it becomes apparent that to probe the intermolecular forces between hydrogen and the adsorbing materials one has to compare the frequency shift of the stretching mode of the adsorbed hydrogen to the frequency of pure hydrogen, hereafter termed "free hydrogen," in the same physical conditions (p,T). When the hydrogen molecules interact with other substances (for example, a foreign gas or an adsorbing material) a further perturbation on the intramolecular potential takes place; such perturbation depends on the relative number and extent of two body interactions (H_2-H_2, H_2-foreign material). For a mixture of hydrogen with foreign gases it was found[40] that the frequency shifts of the Q branch vary linearly with the concentration (C) of hydrogen

$$\boldsymbol{a}_{\text{mixture}} = \boldsymbol{C} \cdot \boldsymbol{a}_{\text{H}_2} + (1 - \boldsymbol{C})\boldsymbol{a}_{\text{foreign gas}}. \tag{5}$$

It is interesting noticing that $a_{\text{foreign gas}}$ is more negative (stronger attractive interactions) for the gases with larger polarizability and positive for weaker attractive interactions such as in the case of helium.

Let us consider, for sake of simplicity, an ideal case of an "isolated" molecule physically adsorbed on a surface; in this case the intramolecular potential will be perturbed only by the intermolecular potential due to the adsorbing material

$$\boldsymbol{V}^{\text{tot}} = \boldsymbol{V}^{\text{Intramolecular}}_{\text{H-H}} + \boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-material}}, \tag{6}$$

$$\boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-material}}(\boldsymbol{r}) = \frac{\boldsymbol{A}^{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-material}}} - \frac{\boldsymbol{B}^{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-material}}}. \tag{7}$$

As in the case of the gaseous molecule even in this case the balance between the attractive and repulsive forces will affect the frequency shift

$$\Delta \boldsymbol{\upsilon}_{\text{H-H}} = \frac{\boldsymbol{K}^{\text{REP}}_{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-material}}} - \frac{\boldsymbol{K}^{\text{ATT}}_{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-material}}}. \tag{8}$$

In this ideal case we should expect that the increased attractive interactions, with respect to the pure gas, will prevail, thus causing a downshift in frequency, as calculated by Frankland and Branner[41] and Canto *et al.*;[42] the effect of the only attractive part of the intermolecular potential on a hydrogen molecule (downshift in frequency) was simulated theoretically by Toffolo *et al.*[43] by means of quantomechanical calculations of H_2 in a static electric field.

This ideal condition ("isolated" adsorbed molecule) was found in an interesting experimental work[32] on hydrogen dissolved in vitreous silica, where almost all hydrogen molecules are trapped in interstices and interact only with the interstice itself.[44]

In practical experimental conditions the intramolecular potential of an adsorbed molecule will be perturbed by, at least, three different intermolecular potentials that account for the interactions (i) with the gaseous molecules, (ii) with the material, and (iii) between molecules in the adsorbed layer

$$\boldsymbol{V}^{\text{tot}} = V^{\text{Intramolecular}}_{\text{H-H}} + \boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-H}_2\text{(gas)}} + \boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-material}} + \boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}, \tag{9}$$

$$\boldsymbol{V}^{\text{Intermolecular}}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}(\boldsymbol{r}) = \frac{\boldsymbol{A}^{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}} - \frac{\boldsymbol{B}^{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}. \tag{10}$$

For a type I isotherm[45] (microporous materials) the relative influence of the last term on the frequency shift [in Eq. (11)] is expected to increase while approaching the saturation of adsorption

$$\Delta \boldsymbol{\upsilon}_{\text{H-H}} = \frac{\boldsymbol{K}^{\text{REP}}_{\text{H}_2\text{(ads)-H}_2\text{(gas)}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-H}_2\text{(gas)}}} - \frac{\boldsymbol{K}^{\text{ATT}}_{\text{H}_2\text{(ads)-H}_2\text{(gas)}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-H}_2\text{(gas)}}} + \frac{\boldsymbol{K}^{\text{REP}}_{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-material}}} - \frac{\boldsymbol{K}^{\text{ATT}}_{\text{H}_2\text{(ads)-material}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-material}}} + \frac{\boldsymbol{K}^{\text{REP}}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}{\boldsymbol{r}^{12}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}} - \frac{\boldsymbol{K}^{\text{ATT}}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}{\boldsymbol{r}^{6}_{\text{H}_2\text{(ads)-H}_2\text{(ads)}}}. \tag{11}$$

If the gas is above its critical temperature only one layer of molecules can be adsorbed on the surface of the material.[46]

The intermolecular potentials due to the interactions with the molecules in the gas phase and within the adsorbed layer are the same, but the effect on the frequency shift is different because the density of the two phases is different. It is obvious that, at a given temperature, the effect of the repulsive part of the intermolecular potential is increased as the density is increased [the term $b_J(T)$ in Eq. (2) is no longer negligible] because the relative population of molecules interacting in the region of the attractive forces decreases relative to the number in the region of the repulsive forces.[34]

Since the aim to use the adsorbing material is to increase the density of the gas with respect to the gaseous phase, in approaching the saturation of adsorption we can expect a tendency toward up-shifted frequencies when compared to the ideal case of an isolated adsorbed molecule.

State of the art of Raman spectroscopy of adsorbed hydrogen on carbon materials

To our knowledge there are only four experimental works dealing with the Raman spectroscopy of adsorbed hydrogen on carbon materials;[24–27] these works focus their attention on carbon nanotubes. Of the three works only the one by Eklund and coauthors[24,25] reports Raman spectra similar to the results obtained in our experimental measurements. These authors recorded the Raman spectrum of H_2, D_2, and HD adsorbed on single wall carbon nanotubes (SWCNT's) and on C_{60} fullerene with a single-grating monochromator. The physical conditions of adsorption reached up to 8 atm and 85 K for hydrogen and deuterium and 5 atm and 85 K for HD. The interpretation of spectrum of hydrogen on SWNT's is carried out based on a deconvolution of lines which indicates both down- and upshifted frequencies with respect to the frequency ascribed to the free gas; the experimental resolution (not reported in their paper) was not sufficient to separate the lines of the Q branch for deuterium. They found unshifted frequencies for a highly oriented pyrolytic graphite and only a downshifted component for C_{60}. Qualitatively, as it will be shown below, the data reported[24,25] are in good agreement with ours, but a word of caution should be spent about the frequency values obtained from band deconvolution when components are very close in frequency.

We found in the literature two theoretical works dealing with the Raman shift in carbon nanotubes.[41,42] Calculations in Ref. 41 are based on a semiclassical model and predict a downshift in frequency for an isolated molecule inside an individual nanotube or in a nanotube rope; the downshift is a function of the diameter of the nanotube: the larger the diameter, the smaller the shift.

Canto and coworkers[42] used a first-principles simulation and obtained results compatible with those by Frankland and Branner,[41] but they identified two contributions to the Raman shift for an isolated molecule inside a nanotube, namely, a downshift for molecules in noncolliding trajectories, and an upshift when the molecules collide with the nanotube. The authors did not dwell on this subject, but the two contributions are clearly due to the perturbations arising from the attractive and repulsive parts of the intermolecular potential [Eq. (8)]. The downshifts predicted by the calculations[41,42] are large, but in normal condition of adsorption (generally 77 K and moderate high pressure); the adsorbed hydrogen molecules interact also with the other molecules in the adsorbed layer, thus the shifts predicted in Refs. 41 and 42 should be taken as a limiting case.

Lee and coauthors[26] measured an upshift of approximately 60 cm^{-1} for hydrogen molecule in SWCNT's charged by electrochemical method; since the peak persists also after annealing at 750 °C they conclude that hydrogen molecules were inside the nanotubes (hydrogen atoms recombined inside the nanotubes). The upshift is determined by the repulsive forces between hydrogen molecules. Strong doubts were cast on these experimental data by Dillon and Heben;[8] Zhang and coauthors[27] ascribed a very weak peak (if any) at 3950 cm^{-1} to the adsorbed hydrogen on multiwall carbon nanotubes. They loaded hydrogen at ambient temperature and 2.0 Mpa (the adsorption of carbon material is almost negligible at room temperature even at high pressure[1,4]); the pressure was kept for two hours and then reduced to the atmospheric value; the material was then fluxed in a helium flow for two hours before obtaining the Raman measurements.

It seems to us very unlikely that one of the less interacting and most diffusive molecules such as hydrogen, even if it could have been adsorbed on the material, could still be there after such treatment and could be detected in a Raman spectrum with 4 cm^{-1} resolution in 60 s.

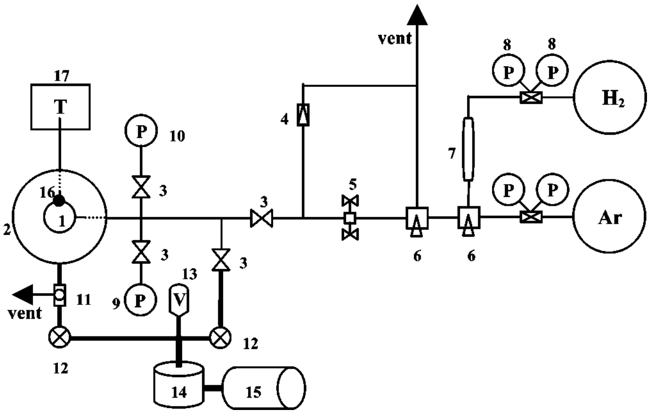

FIG. 1. Scheme of the experimental setup: (1) Raman cell; (2) cryostat; (3) high pressure and high vacuum valves; (4) safety valve; (5) double micrometric valve; (6) three way valves; (7) moisture trap; (8) high pressure manometers (0–200 bar); (9) medium pressure manometer (0–68 bar); (10) low pressure manometer (0–13 bar); (11) vacuum venting valve; (12) vacuum valves; (13) Pirani gauge; (14) turbomolecular pump; (15) rotary pump; and (16) silicon diode (1.5–450 K); (17) heat controller.

III. MATERIALS AND EXPERIMENTS

We have recorded the Raman spectra (Q branch) of adsorbed hydrogen on a commercial amorphous carbon (Norit

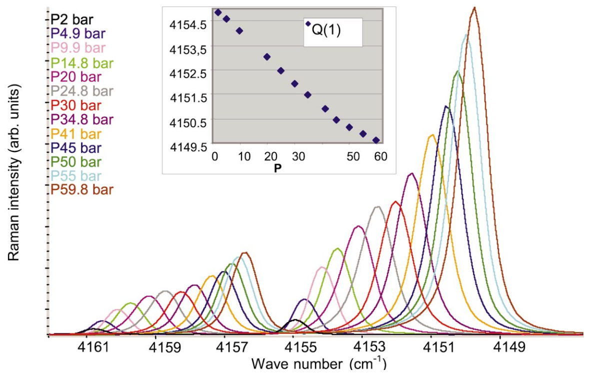

FIG. 2. Raman spectra of gaseous hydrogen at 40±2 K at pressure from 2 to 59.8 bar; in the box the frequencies of the $Q(1)$ line as function of pressure are reported.

TABLE I. Frequencies of $Q(0)$ and $Q(1)$ lines as function of pressure.

P (bar)	Frequency	
	$Q(0)$	$Q(1)$
2.0	4160.88	4154.86
4.9	4160.63	4154.59
9.9	4160.20	4154.08
20.0	4159.27	4153.02
24.8	4158.80	4152.47
30.0	4158.34	4151.94
34.8	4157.95	4151.49
41.0	4157.45	4150.89
45.0	4157.10	4150.45
50.0	4156.86	4150.15
55.0	4156.67	4149.89
59.8	4156.46	4149.63

CASPF) with a high surface area (1674 m^2/g) and on a material obtained by the pyrolysis of hexa-phenyl-benzene at 550 °C for three days (TR21B) that adsorb, respectively, 2,25 wt % (82 K, 5.9 bar) and 0,6 wt % (82 K, 1.5 bar) of hydrogen;[47] the description of the pyrolytic processes and the characterization of the pyrolytic materials are described elsewhere.[48,49]

For recording the experimental spectra we designed and built a special Raman cell that can operate at very low temperatures (40 K) and both in high vacuum or high pressure (up to 100 bars). The cell is placed on a cold finger of a helium closed circuit cryostat (Galileo K1C-ST); an electric resistance and a heat controller allow us to set the desired temperature between 40 K and room temperature (the scheme of the experimental setup is reported in Fig. 1). The Raman spectrum is recorded in a backscattering geometry by focalizing the laser beam (through the quartz window of the cryostat and through the sapphire window of the cell) on the material's surface into the cell by means of an achromatic lens. Raman spectra were recorded with Dilor XY double monochromator in double additive configuration that, with an exciting line of 514.532 nm (Ar/ion laser), can achieve 0.4 cm^{-1} of spectral resolution in the region around 4100 cm^{-1} of Raman shift. The Raman spectra were calibrated with some Ne emission lines in the proximity of the hydrogen Q branch.[50] All samples were kept in high vacuum (10^{-6} mbar) overnight before introducing hydrogen (99.9995%) into the cell. The scheme of the experimental setup is shown in Fig. 1.

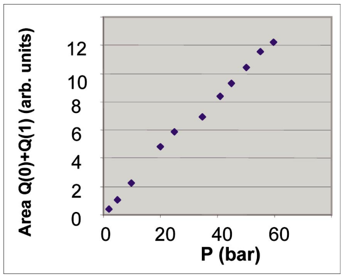

FIG. 3. Plot of the integrated area of $Q(0)+Q(1)$ bands versus pressure; all data are obtained at 40±2 K.

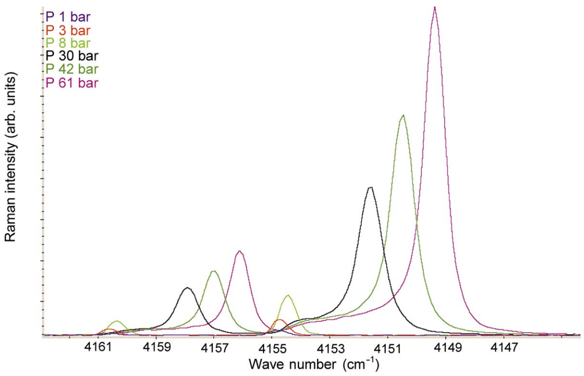

FIG. 4. Raman spectra of hydrogen adsorbed on amorphous carbon at 40±2 K at pressures from 1 to 61 bar.

Experiment

The Raman spectra of free hydrogen show always symmetric lines in all the experimental conditions analyzed (see for example Fig. 2). In Table I the frequencies of the Q branch are reported for free hydrogen at 40 K as function of pressure; Fig. 3 displays the plot of the integrated areas of the two lines.

In Fig. 4 the spectra of adsorbed hydrogen on amorphous carbon at 40 K are reported as a function of pressure; it becomes apparent that the lines are not symmetrical, but downshifted wings appear in the lines up to 8 bar; the lines at 8 bar are almost symmetrical and above 8 bar non-negligible wings appear on the upshifted frequency side. The wings in the spectra are assigned to the adsorbed hydrogen. As already discussed, the upward shift for the adsorbed hydrogen is due to the increase of the repulsive interactions between molecules in the adsorbed layer while approaching the saturation of adsorption.

If we compare the spectra of hydrogen with and without the adsorbing material in the same physical conditions (blue

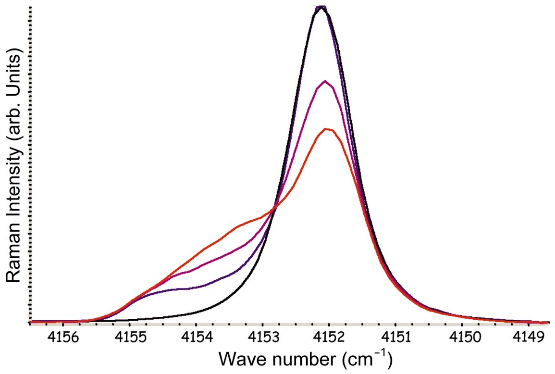

FIG. 5. $Q(1)$ Raman active line of free H_2 at 40 K and 30 bar (black) and $Q(1)$ line of adsorbed hydrogen on amorphous carbon. Blue: 40 K and 30 bar; purple: 39 K and 29 bar; red: 38 K and 28 bar.

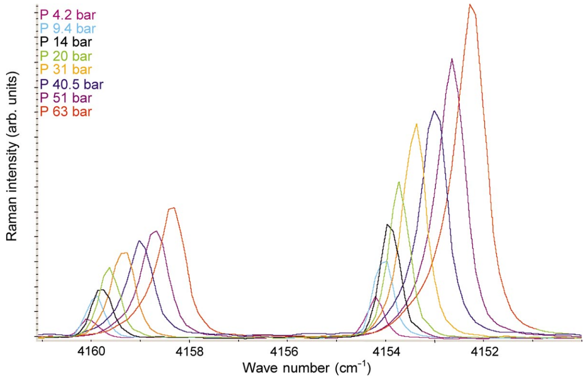

FIG. 6. Raman spectra of hydrogen adsorbed on amorphous carbon at 70±2 K at pressures from 4.2 to 63 bar.

and black spectra in Fig. 5) it becomes apparent that the main peak originates from free hydrogen. It is interesting noticing that a series of spectra (Fig. 5) obtained at 30 bar with temperature reduced from 40 to 38 K (and consequently pressure dropped from 30 to 28 bar) shows an intensity drop of the main peak (free hydrogen) and an increase of the intensity of the upshifted wing (adsorbed molecules).

By increasing the temperature to 70 K we notice downshifted wings up to 20 bars (Fig. 6); above this pressure repulsive interactions within the adsorbed layer start to dominate and generate upshifted frequencies. For the pressure dependent spectra of Figs. 7 and 8 the turning point between upshifted and downshifted wings lies at approximately 150 K at 45 bars (Fig. 7); on the other hand only downshifted frequencies are observed at room temperature up to 64 bars (Fig. 8). By increasing temperature the dispersion in frequency with pressure of the Q branch is reduced and turns out to be very small at ambient temperature.

Because of the small Raman shifts we can conclude that no charge transfer phenomena are involved in the interaction with the adsorbing material, but only a simple physisorption takes place; moreover, no C-H stretching signal in the region of (2800–3300) was detected, thus meaning that chemisorption, if any, should be negligible.

As expected in the case of physisorption, the Raman spectra obtained at different temperatures witness that the higher the temperature, the higher the pressure for achieving the saturation of adsorption.

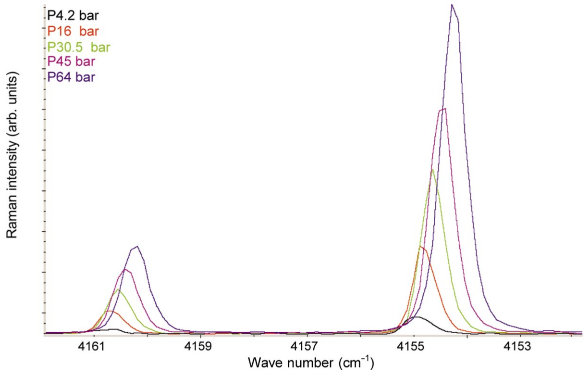

FIG. 7. Raman spectra of hydrogen adsorbed on amorphous carbon at 150±2 K at pressures from 4.2 to 64 bar; $Q(2)$, even if observed in our experiments at lower Raman shifts, is not shown in the spectra for graphic clarity.

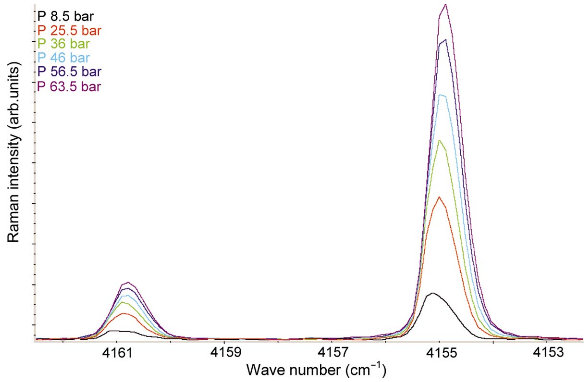

FIG. 8. Raman spectra of hydrogen adsorbed on amorphous carbon at 303±2 K at pressures from 8,5 to 63,5 bar; $Q(2)$ and $Q(3)$, even if observed in our experiments at lower Raman shifts, are not shown in the spectra for graphic clarity.

The spectra of adsorbed hydrogen on TR21B at 40 K as a function of pressure (Fig. 9) show a trend similar to that observed for amorphous carbon, thus showing that similar phenomena take place between hydrogen and the two carbonaceous materials studied.

IV. CONCLUSIONS

We have recorded the Raman spectra of adsorbed hydrogen on two carbon materials (obtained with two independent and chemically different processes) in a variety of different physical conditions. All observations are consistent with a physisorption as a mechanism of adsorption due to van der Waals interactions; no other mechanisms involving stronger interactions with the adsorbing materials (and that, hopefully, could give larger gas adsorption values) appear from the spectra. The lack of attractive interactions, due to the small polarizability of the hydrogen molecule, makes the development of an adsorbing material suitable for automotive application a challenging subject of research. In particular, an adsorbing material with stronger interactions could help in achieving the saturation of adsorption at higher temperature,

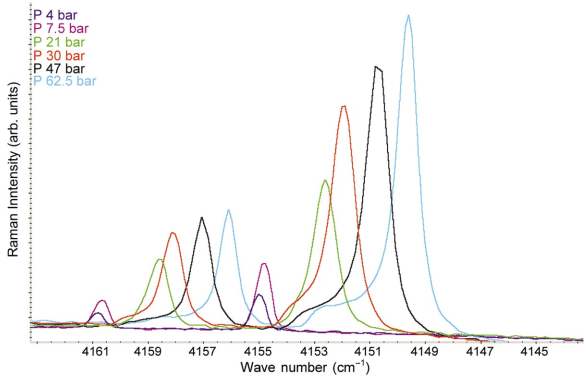

FIG. 9. Raman spectra of hydrogen adsorbed on the pyrolysed sample TR21B at 40±2 K at pressures from 4 to 62.5 bar.

but the surface area will be the main parameter that influences the adsorption values.

A conclusion, very relevant to all efforts to use carbonaceous materials for hydrogen storage, can be drawn from our work. From the physics which derives, based on the data obtained in this work, the large values of hydrogen adsorption on carbon materials at ambient temperature reported in the previous literature should be subjected to a strong critical analysis and possibly the reproducibility of many experiments reported should be checked. We think that in spite of the many optimistic predictions spread in the literature no realistic steps toward a technologically useful absorption of hydrogen on carbonaceous materials have been yet experimentally found.

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[1] M. Hirscher and M. Becher, J. Nanosci. Nanotechnol. **3**, 3 (2003).
[2] A. Züttel, Mater. Today **6**, 24 (2003).
[3] F. Schüth and W. Schmidt, Adv. Eng. Mater. **4**, 269 (2002).
[4] M. Hirscher, M. Becher, M. Haluska, F. von Zeppelin, X. Chen, U. Dettlaff-Weglikowska, and S. Roth, J. Alloys Compd. **356**, 433 (2003).
[5] A. Chambers, C. Park, R. Terry, K. Baker, and N. M. Rodriguez, J. Phys. Chem. B **102**, 4253 (1998).
[6] P. Chen, X. Wu, J. Lin, and K. L. Tan, Science **285**, 91 (1999).
[7] A. C. Dillon, T. Gennet, J. L. Alleman, K. M. Jones, P. A. Parilla, and M. J. Heben, in *Proceedings of the 2000 U.S. DOE Hydrogen Program Review, 2000, NREL/CP-570-28890*.
[8] A. C. Dillon and M. J. Heben, Appl. Phys. A: Mater. Sci. Process. **72**, 133 (2001).
[9] R. Dagani, Chem. Eng. News **80**, 25 (2002).
[10] R. T. Yang, Carbon **38**, 623 (2000).
[11] M. Hirscher, M. Becher, M. Haluska, U. Dettlaff-Weglikowska, A. Quintel, G. S. Duesberg, Y. M. Choi, P. Downes, M. Hulman, S. Roth, I. Stepanek, and P. Bernier, Appl. Phys. A: Mater. Sci. Process. **72**, 129 (2001).
[12] M. Hirscher, M. Becher, M. Haluska, A. Quintel, V. Shakalova, Y. M. Choi, U. Dettlaff-Weglikowska, S. Roth, I. Stepanek, P. Bernier, A. Leonhardt, and J. Fink, J. Alloys Compd. **330**, 654 (2002).
[13] M. Haluska, M. Hirsher, M. Becher, U. Dettlaff-Weglikowska, X. Chen, and S. Roth, Mater. Sci. Eng., B **108**, 130 (2004).
[14] L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001).
[15] A. Züttel, P. Sudan, P. Mauron, T. Kiyobayashi, C. Emmenegger, and L. Schlapbach, Int. J. Hydrogen Energy **25**, 203 (2002).
[16] A. Züttel, C. Nützenadel, P. Sudan, P. Mauron, C. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, and T. Kiyobayashi, J. Alloys Compd. **330**, 654 (2002).
[17] T. Kiyobayashi, H. T. Takeshita, H. Tanaka, N. Takeichi, A. Züttel, L. Schlapbach, and N. Kuriyama, J. Alloys Compd. **330**, 666 (2002).
[18] X. B. Wu, P. Chen, J. Lin, and K. L. Tan, Int. J. Hydrogen Energy **25**, 261 (2000).
[19] G. P. Dai, C. Liu, M. Liu, M. Z. Wang, and H. M. Cheng, Nano Lett. **2**, 503 (2002).
[20] L. Zhou, Y. Zhou, and Y. Sun, Int. J. Hydrogen Energy **29**, 475 (2004).
[21] H. Takagi, H. Hatori, Y. Soneda, N. Yoshizawa, and Y. Yamada, Mater. Sci. Eng., B **108**, 143 (2004).
[22] C. Zhang, X. Lu, and A. Gu, Int. J. Hydrogen Energy **29**, 1271 (2004).
[23] C. M. Brown, T. Yildirim, D. A. Neumann, M. J. Heben, T. Gennet, A. C. Dillon, J. L. Alleman, and J. E. Fischer, Chem. Phys. Lett. **329**, 311 (2000).
[24] B. K. Pradhan, G. U. Sumanasekera, K. W. Adu, H. E. Romaro, K. A. Williams, and P. C. Eklund, Physica B **323**, 115 (2002).
[25] K. A. Williams, B. K. Pradhan, P. C. Eklund, M. K. Kostov, and M. W. Cole, Phys. Rev. Lett. **88**, 165502 (2002).
[26] S. M. Lee, K. S. Park, Y. C. Choi, Y. S. Park, J. M. Bok, D. J. Bae, K. S. Nahm, Y. G. Choi, S. C. Yu, N. Kim, T. Frauenheim, and Y. H. Lee, Synth. Met. **113**, 209 (2000).
[27] H. B. Zhang, G. D. Lin, Z. H. Zhou, X. Dong, and T. Chen, Carbon **40**, 2429 (2002).
[28] R. N. Jones and C. Sandorfy, *Chemical Applications of Spectroscopy*, in Techniques of Organic Chemistry, Vol. IX, edited by A. Weissberger (Interscience, New York, 1956).
[29] M. Zander, *Polycycliche Aromaten* (Teubner, Stuttgart, 1995).
[30] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Methuen and Co., London, 1959).
[31] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts* (Wiley, New York, 2001).
[32] F. Rasetti, Phys. Rev. **34**, 367 (1929).
[33] G. H. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand Company, New York, 1950) pp. 100, 101, 438, 439.
[34] A. D. May, G. Varghese, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **42**, 1058 (1964).
[35] E. C. Looi, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **56**, 1102 (1978).
[36] G. Tead and G. E. Macwood, J. Chem. Phys. **3**, 760 (1935).
[37] W. K. Bischel and M. J. Dyer, Phys. Rev. A **33**, 3113 (1986).
[38] E. Gregoryanz, A. F. Goncharov, K. Matsuishi, H. K. Mao, and R. J. Hemley, Phys. Rev. Lett. **90**, 175701 (2003).
[39] H. Mao and R. Hemley, Rev. Mod. Phys. **66**, 671 (1994).
[40] P. Lallemand and P. Simova, J. Mol. Spectrosc. **26**, 262 (1968).
[41] S. J. V. Frankland and D. W. Branner, Chem. Phys. Lett. **334**, 18 (2001).

[42] G. Canto, P. Ordejon, H. Cheng, A. C. Cooper, and G. P. Pez, New J. Phys. **5**, 124 (2003).
[43] F. Toffolo, M. Tommasini, M. Del Zoppo, and G. Zerbi Chem. Phys. Lett. **405**, 108 (2005).
[44] C. M. Hartwig and J. Vitko Jr., Phys. Rev. B **18**, 3006 (1978).
[45] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, Pure Appl. Chem. **57**, 603 (1985).
[46] S. Brunauer, P. H. Hemmet, and E. Teller, J. Am. Chem. Soc. **62**, 309 (1938).
[47] L. Gherardi (private communication).
[48] A. Centrone, L. Brambilla, T. Renouard, L. Gherghel, C. Mathis, K. Müllen, and G. Zerbi, Carbon **43** (2005).
[49] T. Renouard, L. Gherghel, M. Wachtler, F. Bonino, R. Nuffer, B. Scrosati, C. Mathis, and K. Muellen, J. Power Sources **139**, 242 (2005).
[50] *Handbook of Chemistry and Physics*, edited by D. R. Lide, 71st ed. (CRC, Boston, 1990).