

Induced infrared absorption of molecular hydrogen in solid C₆₀

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(Received 8 January 2002; published 28 March 2002)

We report on the observation of induced infrared absorption in a molecular species trapped within a C₆₀ lattice. Infrared spectra for interstitial H₂ show distinct rotational and translational side-bands superimposed on the H₂'s highly redshifted (54 cm⁻¹) fundamental vibrational mode. Data indicate that the hydrogen is rotating almost completely freely while at the same time undergoing localized three-dimensional translational motion within the "box" formed by the C₆₀ molecules.

DOI: 10.1103/PhysRevB.65.140302

PACS number(s): 68.43.-h, 68.43.Pq, 78.30.Na

It is well known that as solid C₆₀ is cooled to 260 K it undergoes an orientational phase transition from a structure in which the molecules freely rotate to one in which they undergo a ratcheting motion between orientationally equivalent positions.¹ Theoretical models could only explain the main features (e.g., temperature) of this transition by proposing *ad hoc* coulombic forces to supplement the graphitelike intermolecular interactions.² To date, we still lack a comprehensive understanding of the C₆₀ intermolecular potential whose importance was very recently illustrated by the discovery of superconductivity at 117 K within a doped C₆₀ lattice.³

The use of infrared (IR) spectroscopy of trapped probe molecules to study the C₆₀ intermolecular potential was first demonstrated in the pioneering work of Holleman *et al.*⁴ They showed that the redshifted vibrational spectrum of CO trapped within the C₆₀ octahedral (O_h) interstitial site could be explained by modeling the CO interactions with the surrounding C₆₀ molecules. They also offered the exciting suggestion that these voids would provide the ideal setting for studying quantized motion analogous to a particle in a box. The highly uniform, well-separated voids are just large enough to accept a single molecule acted upon by weak van der Waals interactions. However, despite IR studies on more than half a dozen different species, no one has yet shown evidence for quantized translational motion associated with the trapped molecules.⁴⁻⁶

By far the most interesting candidate to observe in these types of studies is molecular hydrogen. Due to its small mass, the rotational and translational sidebands are expected to be well separated from the main vibrational peak. In addition, there is presently great practical interest in the storage of molecular hydrogen within novel forms of carbon.^{7,8} In an earlier paper,⁹ we used neutron diffraction to show that under moderate loading pressures molecular hydrogen occupies a substantial fraction of the C₆₀ O_h interstitial sites. Because H₂ has no dipole moment, observing its IR signal is challenging; any IR absorption arises solely through interactions with the C₆₀ lattice. Traditional methods using C₆₀ thin films do not lead to a sufficient optical path length to detect the induced absorption. Samples cannot be made any thicker because the fullerene material itself would then scatter too much of the light. In this paper, we show how the technique of diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) is ideally suited for observing weak impurity

modes in an intrinsically transparent but highly scattering host such as C₆₀. Data taken while maintaining a constant loading pressure allow us to monitor the rate at which the H₂ diffuses into the C₆₀ lattice. These spectra exhibit rotational and translational sidebands superimposed on the highly redshifted vibrational mode of the trapped H₂ molecules. As we will show, the frequencies for all three types of excitations are consistent with existing theoretical predictions⁹ and lead us to speculate that the C₆₀ grains may have a quasifluidlike surface layer.

We first determined the binding energy of H₂ within the O_h site through a series of isotherm measurements. The C₆₀ powder obtained commercially from MER Corporation was initially heated under vacuum at 450 K for two days to remove any residual solvent. The powder was also evacuated *in situ* at elevated temperature to remove any preadsorbed gases. The hydrogen loading pressure was maintained for several hours to assure that equilibrium had been reached. The sample cell was then quenched rapidly with liquid nitrogen, kinetically locking the H₂ within the lattice.¹⁰ The loading pressure was removed and the quantity of physisorbed hydrogen determined by warming the sample back to room temperature and monitoring the outgassing pressure within a known volume.

Figure 1 shows the isotherm curve obtained at 273 K. In

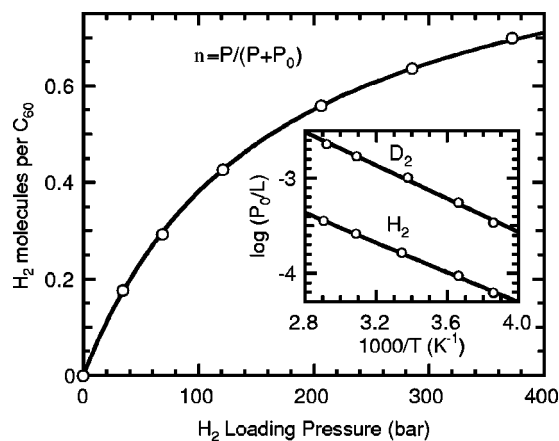


FIG. 1. Loading isotherm for H₂ in C₆₀ at 273 K. Data are fit to the one-parameter Langmuir model with P₀ = 160 bar. The inset shows the Arrhenius plot of modified P₀ for both H₂ and D₂. Data were taken between 350 and 260 K.

contrast to previous studies^{11,12} these results show almost perfect agreement with the standard Langmuir isotherm, $n = P/(P+P_0)$, where n is the fraction of the available sites filled, P is the pressure of the gas, and P_0 is a characteristic pressure determined by the interactions of the gas-host system. The isotherm data asymptotically approach 1.0 ± 0.05 H₂ per C₆₀ in agreement with the fact that the lattice contains one O_h site per C₆₀ molecule. This confirms that there is no significant trapping of the H₂ within the grain boundaries of the powder. For an ideal gas, it is known that within the Langmuir model¹³

$$P_0 = \frac{k_B T}{V_G} \frac{Z_G}{Z_A}, \quad (1)$$

where T is the temperature, V_G is the gas volume, and Z_G and Z_A are the partition functions of the gas and the adsorbed species respectively. The C₆₀ potential causes only small changes to the hydrogen's internal degrees of freedom and so to a good approximation $Z_A^{int} = Z_G^{int}$. Thus,

$$P_0 = \left(\frac{M}{2\pi\hbar^2} \right)^{3/2} (k_B T)^{5/2} [1 - e^{-\hbar\omega/k_B T}]^3 e^{-E_b/k_B T} \\ = L(T) e^{-E_b/k_B T}, \quad (2)$$

where E_b represents the energy difference between the gas molecule at rest and the bound molecule at its zero-point-energy, and we have assumed the trapped molecule undergoes three-dimensional isotropic simple-harmonic motion with translational frequency determined by our own IR measurements. Within the measured temperature regime the defined quantity $L(T)$ produces only a small correction to the standard Arrhenius approach, in which the temperature dependence of the preexponential factor is ignored completely. From the slope of the inset in Fig. 1 we obtain values for E_b of 68 and 75 meV for H₂ and D₂, respectively. The slightly greater binding energy for D₂ arises from its smaller zero point energy. Adding on the zero-point energy of $3/2\hbar\omega$ (24 and 17 meV for H₂ and D₂, respectively) yields an adsorption well depth of 92 meV. This compares well with the theoretically predicted value of 102 meV.⁹

The IR spectra were taken using a Bomem DA3 spectrometer with a liquid-nitrogen-cooled MCT detector and KBr beamsplitter. The DRIFTS accessory included a ZnSe dome that allowed spectra to be taken with gas pressures as high as 100 bar. Figure 2 shows a series of room temperature spectra taken while subjecting the C₆₀ powder to H₂ at a loading pressure of 70 bars. The spectra, referenced to that of the pure C₆₀, contain a series of bands in the region of the H₂ fundamental vibrational mode at 4161 cm⁻¹. The bands grow in intensity as the hydrogen gas slowly diffuses into the C₆₀ lattice. The time constant for this process agrees closely with unloading results obtained using proton NMR.¹⁴

The bands in the successive spectra appear to scale in intensity without any broadening, shifting, or splitting of the peaks with increasing hydrogen concentration. The smaller features marked with arrows appear to reach saturation with a somewhat faster time constant; however, the overlapping

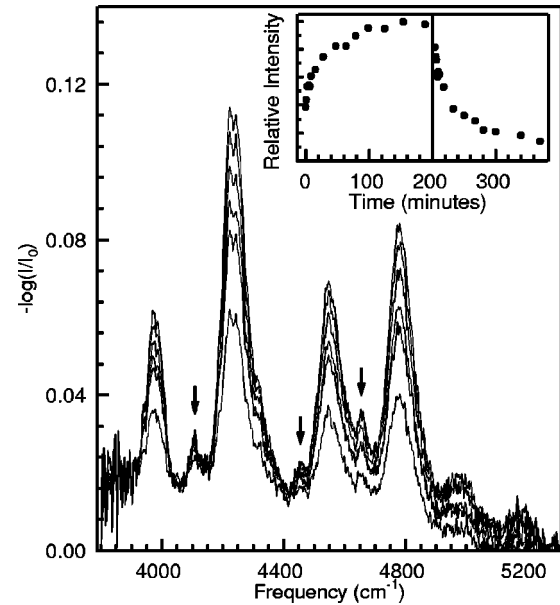


FIG. 2. Room temperature DRIFTS spectra of H₂ in C₆₀. The spectra taken at 4 cm⁻¹ resolution are referenced to that of pure C₆₀ and are taken with a H₂ loading pressure of 70 bars. After 200 min the loading pressure is released. The inset shows the integrated sum of all the H₂ bands between 3800 and 5300 cm⁻¹.

nature of the peaks makes it difficult to deconvolute the individual intensities. The inset shows the sum of the integrated intensity for all of the bands as a function of time. After 200 min the system had reached equilibrium, at which point the loading pressure was removed and the H₂ allowed to diffuse out of the sample. In contrast with results reported for neon,¹⁵ we see no major difference between the kinetics for loading and unloading. The intensity of the peaks shows a rapid initial change followed by a much slower tail towards equilibrium. Similar two time-constant kinetics have been observed for oxygen diffusing into the C₆₀ lattice.¹⁶

Neglecting rotational distortion effects, the energy of a free hydrogen molecule in its electronic ground state can be written as

$$E_{\nu,J} = (\nu + 1/2)\nu_0 + B_\nu J(J+1), \quad (3)$$

where ν and J are, respectively, the vibrational and rotational quantum numbers, $\nu_0 = 4161$ cm⁻¹, and the rotational constant $B_\nu = 59$ and 56 cm⁻¹ for hydrogen in its ground and first vibrational excited states respectively.¹⁷ Quantum statistics constrain orthohydrogen with total nuclear spin 1 to have odd values of J , and parahydrogen with total nuclear spin 0 to have even values J . Therefore the selection rules for photon-induced transitions are $\Delta J = 0$ (Q transitions) and $\Delta J = \pm 2$ (S and O transitions).

Figure 3 shows our assignment of the bands in the C₆₀-induced H₂ spectrum. The pattern contains a series of weak central peaks with much stronger bands symmetrically spaced on either side. The central Q bands arise from pure rotational-vibrational transitions while the symmetrical splitting of the sidebands indicates that they arise from creation (R branch) or annihilation (P branch) of localized transla-

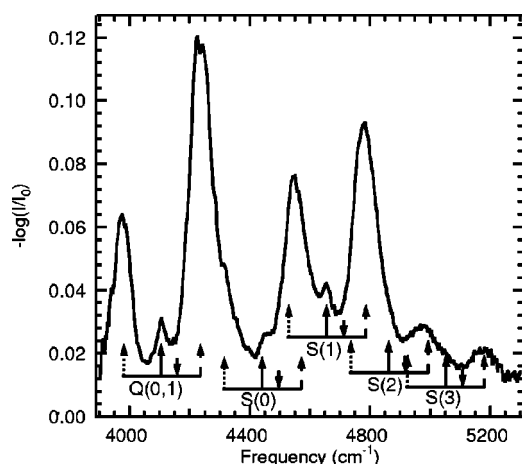


FIG. 3. Mode assignment for the C_{60} -induced H_2 bands. Dotted arrows indicate P transitions, solid arrows Q transitions, and dashed arrows R transitions. The arrows pointing down show the known location of the H_2 gas phase modes. In all cases the translational sidebands (P and R) are shown at ± 127 cm^{-1} relative to the pure rotational-vibrational modes (Q), which are each redshifted by 54 cm^{-1} relative to the gas phase. For the $S(2)$ and $S(3)$ transitions only the R -branch transitions are strong enough to be observed.

tional modes of the trapped H_2 . In all cases, the translational sidebands are shown at ± 127 cm^{-1} , in good agreement with theoretical estimates⁹ on the order of 110 cm^{-1} . There is also evidence (most notably in the Q_R band) of an 18 cm^{-1} splitting in the translational sidebands which may be due to crystal-field effects.

The O transitions ($\Delta J = -2$) that occur at frequencies below 3800 cm^{-1} and are significantly reduced in intensity relative to the S transitions could not be observed due to the presence of overlapping water bands. The $Q(0)$ and $Q(1)$ transitions that differ by 6 cm^{-1} in the gas phase are not resolved. As shown in Fig. 3, for each of the observed modes [$Q(0,1)$, $S(0)$, $S(1)$, $S(2)$, and $S(3)$], our assignment has the central pure vibrational-rotational branch shifted in frequency by the same amount, 54 cm^{-1} , relative to the known values for gas phase H_2 .¹⁷ This indicates that the hydrogen is rotating almost completely freely within the interstitial O_h site with no detectable change in the rotational energy levels relative to the gas phase. This is not surprising, since the binding potential is predicted to have a small angular corrugation of only a few meV in comparison to the translational zero-point energy in excess of 20 meV.⁹

When we repeated the DRIFTS experiment with D_2 , which has a reduced vibrational frequency, the presence of strong C_{60} absorption bands meant that we could only identify 3 induced D_2 modes. These indicated a vibrational redshift of 38 cm^{-1} and translational frequency of 90 cm^{-1} , both of which are in agreement with the expected $\sqrt{2}$ isotope effect. The 54 cm^{-1} redshift of the H_2 vibrational frequency is somewhat larger than values reported for substitutional H_2 in rare gas matrices which range from 19 cm^{-1} for Ar to 38 cm^{-1} for Xe.¹⁸ We can estimate the expected shift in our case by noting that for a highly isotropic potential, the fre-

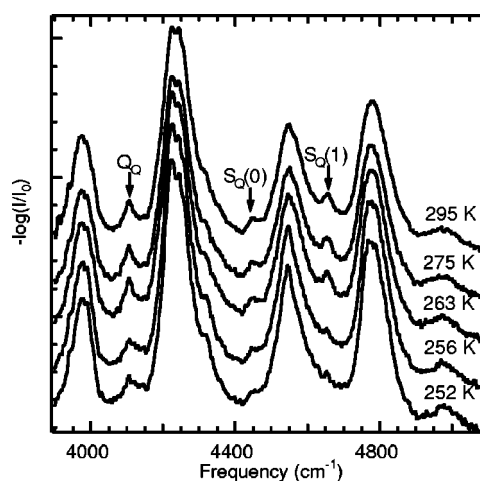


FIG. 4. Temperature dependence of the induced H_2 spectrum. The Q bands indicated by the arrows show a sharp decrease in intensity on cooling through the C_{60} phase transition.

quency shift arises mainly from changes in the molecular polarizability of H_2 between the ground and first excited vibrational state.¹⁹ Essentially, the binding energy in the excited state is greater than that in the ground state due to its slightly increased polarizability. Using the *ab initio* determined values for the molecular polarizability of unperturbed H_2 and D_2 (Ref. 20) and the binding energies obtained from our isotherm measurements, we predict redshifts of 62 and 44 cm^{-1} for H_2 and D_2 , respectively. These compare quite well with our observed values of 54 and 38 cm^{-1} .

With the DRIFTS technique it is extremely difficult to obtain anything more than a qualitative explanation of the absorption intensities. However, we note that the ratio of R to P branch intensity is consistent with the detailed balance prediction of $\approx 2:1$ at room temperature. Similarly the reduced intensity of the $S(2)$ and $S(3)$ bands arises because the ground states associated with these transitions are not significantly populated at room temperature.

The most surprising aspect of the spectrum shown in Fig. 3 is the presence of weak purely rotational-vibrational central Q bands (zero-phonon). An H_2 molecule trapped within an O_h site experiences a centrosymmetric potential which cannot produce IR activity in these modes.²¹ For example, in the face-centered-cubic phase of solid hydrogen only the translational sidebands are activated.²² In our case the Q transitions could be activated by impurities, lattice defects, or a lack of local O_h symmetry for the interstitial site. On the rapid time scale of the H_2 vibration the C_{60} molecules must be considered as stationary objects, thus modifying the local octahedral symmetry.

To distinguish between these explanations we obtained a series of spectra while cooling the system to its base temperature of 250 K. As shown in Fig. 4, cooling the sample to 263 K produced only minor changes in the overall spectrum. The only clear effect is that the lower frequency peak of the Q_R doublet becomes more intense, consistent with the changing Boltzmann population of an 18 cm^{-1} split ground state. Cooling the sample below the 260 K phase transition

produced a sudden decrease in the intensity of all the central Q bands, most notably the $S_Q(0)$ band which disappeared almost entirely.

These results rule out both impurities and lack of true O_h symmetry as the origin of the Q bands. In fact it is quite interesting to observe the decrease the intensity of a band caused by a transition to a lower symmetry state, which would be expected to enhance its mode strength. We now speculate that the Q transitions may be caused by the presence of C_{60} lattice vacancies and adatoms. Recent neutron spin echo data have shown evidence for a quasifluidlike surface layer in which C_{60} vacancies are highly mobile.²³ The mobility is strongest just above the phase transition and dies out for lower temperature. This behavior might also explain the two time-constant kinetics observed by several groups for the loading and unloading of gases into C_{60} . Rapid loading occurs within the surface fluid layer of a grain followed by much slower diffusion into the bulk. Morosin *et al.*¹⁵ have

also reported a sudden decrease in the loading kinetics of neon on cooling through the phase transition.

In conclusion, we have shown that IR diffuse reflectance is an ideal technique for observing the quantum dynamics of gas molecules trapped within a C_{60} lattice. The same technique should work equally well with nanotubes or other novel forms of carbon. Data reveal essentially free rotational motion of the translationally bound H_2 superimposed on a highly redshifted vibrational mode. The frequencies of all three types of excitations are consistent with simplified theoretical calculations and should provide accurate benchmarks for any complete theoretical model of the C_{60} intermolecular potential.

This work was supported by Research Corporation Grant No. CC5240 and PRF Grant No. 35452-GB. We would like to acknowledge D. Sethna and Z. Szuts for their work on the high-pressure system and Y. Ijiri, J. Yates, A. McDowell, N. Craig, D. Neumann, and T. Yildirim for helpful discussions.

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¹M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

²S.L. Chaplot and L. Pintschovius, *Int. J. Mod. Phys. B* **13**, 217 (1999).

³J.H. Schon, C. Kloc, and B. Batlogg, *Science* **293**, 2432 (2001).

⁴I. Holleman, G. von Helden, E.H.T. Olthof, P.J.M. van Bentum, R. Engeln, G.H. Nachttegaal, A.P.M. Kentgens, B. H. Meier, A. van der Avoird, and G. Meijer, *Phys. Rev. Lett.* **79**, 1138 (1997).

⁵G.E. Gadd, M. James, S. Moricca, D. Cassidy, P.J. Evans, B. Collins, and R.S. Armstrong, *J. Phys. Chem. Solids* **59**, 1383 (1998).

⁶G.E. Gadd, P.J. Evans, S. Kennedy, M. James, M. Elcombe, D. Cassidy, S. Moricca, J. Holmes, N. Webb, and A. Dixon, *Fullerene Sci. Technol.* **7**, 1043 (1999).

⁷C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, and M.S. Dresselhaus, *Science* **286**, 1127 (1999).

⁸Y. Ye, C.C. Ahn, B. Fultz, J.J. Vajo, and J.J. Zinc, *Appl. Phys. Lett.* **77**, 2171 (2000).

⁹S.A. FitzGerald, T. Yildirim, L.J. Santodonato, D.A. Neumann, J.R.D. Copley, J.J. Rush, and F. Trouw, *Phys. Rev. B* **60**, 6439 (1999).

¹⁰A.I. Kolesnikov, V.E. Antonov, I.O. Bashkin, E.G. Ponyatovsky, A.Y. Muzychka, A.P. Moravsky, G. Grosse, and F.E. Wagner, *Physica B* **234**, 10 (1997).

¹¹B. Morosin, J.D. Jorgensen, S. Short, G.H. Kwei, and J.E. Schirber, *Phys. Rev. B* **53**, 1675 (1996).

¹²Good agreement with the Langmuir model is extremely sensitive on measuring the absolute volume of the outgassing cell. In our earlier paper (Ref. 9) we inaccurately measured this volume, leading us to mistakenly conclude that the isotherm did not follow the Langmuir predictions.

¹³V. Bortolani, N.H. March, and M.P. Tosi, *Interaction of Atoms and Molecules with Solid Surfaces* (Plenum Press, New York, 1990).

¹⁴R. Assink, J.E. Schirber, D. Loy, B. Morosin, and G. Carlson, *J. Mater. Res.* **7**, 2136 (1992).

¹⁵B. Morosin, Z. Hu, J.D. Jorgensen, S. Short, J.E. Schirber, and G.H. Kwei, *Phys. Rev. B* **59**, 6051 (1999).

¹⁶E.A. Katz, A.I. Shames, D. Faiman, S. Shtutina, Y. Cohen, S. Goren, W. Kempinski, and L. Piekara-Sady, *Physica B* **273**, 934 (1999).

¹⁷S.L. Bragg, J.W. Brault, and W.H. Smith, *Astrophys. J.* **263**, 999 (1982).

¹⁸M.E. Alikhani, B. Silvi, and J.P. Perchard, *J. Chem. Phys.* **90**, 5221 (1989).

¹⁹D.M. Bishop, *J. Chem. Phys.* **98**, 3179 (1993).

²⁰W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

²¹G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company Inc., New York, 1996).

²²J.V. Kranendonk, *Solid Hydrogen: Theory of the Properties of Solid H_2 , HD , and D_2* (Plenum Press, New York, 1983).

²³V.T. Lebedev, D.N. Orlova, A.I. Sibilev, G. Torok, L. Cser, V.P. Budtov, and A.V. Polyakov, *Mol. Mater.* **13**, 123 (2000).