

Cryogenic apparatus for diffuse reflection infrared spectroscopy with high-pressure capabilities

S. A. FitzGerald, H. O. H. Churchill, P. M. Korngut, C. B. Simmons, and Y. E. Strangas
Department of Physics and Astronomy, Oberlin College, Oberlin, Ohio 44074

(Received 12 May 2006; accepted 7 August 2006; published online 25 September 2006)

A cryogenic apparatus for obtaining diffuse reflection infrared spectra at liquid helium temperature is described. The system combines a commercially available reflection accessory and cold finger cryostat with a custom designed vacuum housing and high-pressure sample cell. This enables spectra to be obtained from room temperature to 10 K and at gas loading pressures as high as 100 bars. Initial experiments on H₂ in solid C₆₀ show the power of the system to obtain spectra that are significantly enhanced relative to those at room temperature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2349289]

I. INTRODUCTION

There is presently much interest in hydrogen storage for fuel cell applications.¹⁻³ The ultimate goal of this research is to obtain a light-weight matrix that could hold significant quantities of molecular hydrogen at room temperature. In trying to develop these materials it is essential that researchers determine the type of site where the hydrogen binds to the matrix and the nature of the intermolecular interaction that holds it in place.

Infrared spectroscopy has been traditionally a powerful tool for probing the intermolecular interactions between a host and an adsorbate.⁴ The necessary information is obtained by measuring changes in the rotational-vibrational spectrum of the adsorbate when it binds to the host. In most cases the spectra are obtained through standard transmission measurements. Unfortunately this technique cannot be readily applied to a diverse range of new materials such as carbon nanotubes, fullerenes, and metal-organic frameworks that show great promise for hydrogen storage.⁵ The materials exist either as powders that scatter too much light for transmission measurements or as films that are far too thin to produce significant signal from the extremely weak infrared activity of an adsorbed hydrogen molecule.

In this article we show how the technique of diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) is ideally suited to this type of problem. Diffuse reflectivity has been used for more than 50 years to obtain spectra on highly scattering samples such as powders.⁶ The radiation is focused onto a sample with a roughened surface to minimize unwanted specular reflection. The radiation then penetrates into the sample and undergoes multiple scattering events between grains before either being absorbed or reemerging at some random angle. This emerging radiation is focused onto a detector using collecting optics. Dips in the resulting spectrum indicate the frequencies at which the radiation was absorbed.

In the ideal case the host material has negligible absorption at the infrared frequency of interest. Thus a quite long effective optical path length can be achieved within the

sample making it possible to observe an extremely weak infrared signal from an adsorbate such as molecular hydrogen. If spectra with the adsorbate in place are referenced to the pure host then in principle the vibrational-rotational spectrum of just the trapped adsorbate is obtained.

Given these advantages it is surprising that to date the DRIFTS technique has been used sparingly to investigate adsorbed hydrogen.⁷ One of the drawbacks of DRIFTS is that the large collecting optics make it quite difficult to obtain data at liquid helium temperature. Unfortunately, many systems of interest only adsorb large quantities of hydrogen at low temperature and even if adsorption can be obtained at room temperature the spectra tend to be quite broad with multiple overlapping peaks.⁸ As such data interpretation is difficult at best with large uncertainties.

Below we describe an apparatus for obtaining DRIFT spectra at temperatures from ambient to liquid helium. Our system places a commercially available DRIFTS accessory within a custom built vacuum housing. The sample cell with high-pressure capabilities is mounted to the end of a specially designed cryogenic cold finger. Although our motivation for this work is to study adsorbed hydrogen, the apparatus can be used for any gas adsorbate, or for that matter for any standard DRIFTS application. In addition to cryogenic capabilities the apparatus also allows gas to be added to the system at pressures up to 100 bars. In the next section we describe the main parts of the apparatus. The performance of the system in conjunction with a Bomem DA3 spectrometer is summarized in Sec. III. Finally, we present some initial data obtained on H₂ adsorbed within C₆₀ powders. These results illustrate the dramatic improvement in the spectra when measurements are obtained at liquid helium temperature.

II. APPARATUS

Figure 1 shows a schematic representation of the apparatus. It comprises a main vacuum chamber housing the cryogenic cold finger, sample mount with high-pressure

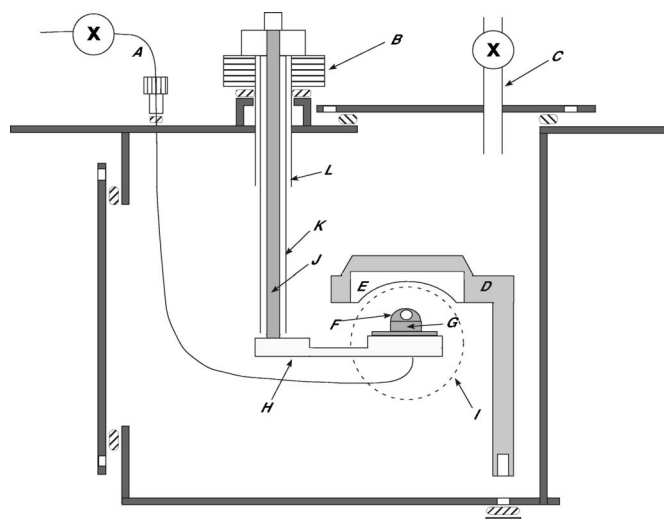


FIG. 1. Schematic of cryogenically cooled DRIFTS accessory: (A) high-pressure gas line, (B) sample height adjuster, (C) evacuation line, (D) DRIFTS mount, (E) ellipsoidal mirror, (F) high-pressure dome, (G) sample cup, (H) copper slab, (I) CaF_2 window, (J) cold finger, (K) radiation shield, and (L) cutoff vacuum wall.

dome, and DRIFTS optics. Infrared radiation from the spectrometer enters and exits the apparatus through CaF_2 windows in the front and rear of the chamber.

The vacuum chamber consists of a welded aluminum box ($15 \times 12 \times 15 \text{ cm}^3$) with removable side and lid panels. These are necessary to provide access for mounting the different components within the chamber. The panels are attached using standard rubber o-ring seals. Similarly the CaF_2 windows are press sealed against rubber o-rings. Although the system was designed to work in the mid infrared it could easily be extended to the near or far infrared by replacing the CaF_2 windows with either quartz or polyethylene. Evacuation of the chamber is achieved through a port in the lid. Both the high-pressure gas line and cold finger cryostat enter via compression seals in the top plate.

The cold finger is a modified model ST-300T continuous flow cryostat purchased from Janis Research Company. For our purposes the bottom section was removed and the outer vacuum wall cut off 10 cm above the sample mount. Vacuum between the inner and outer walls of the cryostat is achieved by evacuating the entire vacuum chamber. The cryostat sample mount consists of a copper rod (diameter of 2.25 cm) wrapped with a 25Ω heater and silicon diode temperature sensor. Before modification the cryostat had an advertised operating range from 2 to 325 K.

A 6 mm thick copper slab of length of 10 cm with a 6 mm diameter copper rod soldered at the far end is bolted to the base of the cryostat sample mount. The sample powder is placed in a recess cup at the top of the rod. The outside of the rod is tapered and covered with an absorbing black paint to minimize unwanted reflection. The high-pressure gas enters the cell through a 3 mm diameter tube soldered onto the underside of the copper slab.

The DRIFTS optics consisting of a modified "Collector" assembly purchased from Spectra-Tech Inc. is bolted to the bottom of the vacuum chamber. The mounting bolts are covered by caps that are o-ring sealed to the underside of the

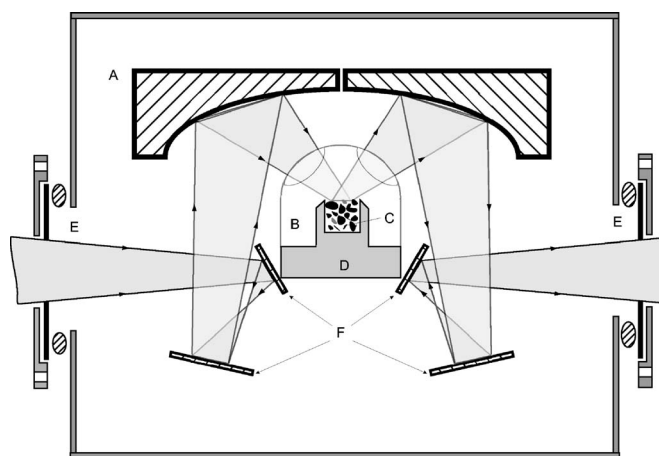


FIG. 2. Schematic of radiation propagation within vacuum chamber: (A) ellipsoidal mirrors, (B) high-pressure dome, (C) sample, (D) copper sample cup, (E) CaF_2 windows, and (F) plane mirrors.

base. Figure 2 shows the basic working of the DRIFTS optics. The incident radiation is reflected onto off-axis ellipsoidal mirrors that focus the beam through the window of the high-pressure dome and onto the sample. Within the sample the radiation undergoes multiple scattering events before reemerging at some random angle. The second ellipsoidal mirror collects up to 50% of the emerging radiation and passes it out of the chamber to be focused onto the detector via additional optics.

As shown in Fig. 2, the sample can be enclosed by a high-pressure dome with optical access for infrared radiation to enter and exit. The dome windows are made of 3 mm thick sapphire brazed onto a titanium retainer ring. This was in turn brazed onto the cell through the openings in the walls machined out at a 45° angle. The dome assembly was brazed onto a stainless-steel base that is sealed onto the copper slab using an indium o-ring. The cell has a nominal pressure rating of 100 bars although it is believed that substantially higher pressure could be achieved.

III. PROCEDURE

All spectra were obtained using a Bomem DA3 Michelson interferometer with Globar source and KBr beam splitter. We used a liquid nitrogen cooled mercury cadmium telluride detector with a peak detectivity of $3 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{-1}$. The spectrometer has a maximum resolution of 0.04 cm^{-1} , but 0.2 cm^{-1} was the highest value used in our initial tests.

The spectrometer has a large sample compartment making it possible to simply mount the vacuum chamber within the spectrometer (requiring no additional optics). Before cool down the chamber is evacuated to a pressure of less than 10^{-5} mbar. The sample is cooled by continuously transferring liquid helium from a storage dewar to the cold finger cryostat. During the initial cool down and at the base temperature the exhaust from the cryostat is evacuated using a mechanical pump. Otherwise it is allowed to vent into the air. It takes 15 min for the system to cool from ambient to a base temperature of 10 K. This time agrees with the nominal

value listed by the manufacturer for the unmodified cryostat. At the base temperature the system consumes helium at a rate of roughly 1 l/h.

Temperature is determined using two matched silicon diode thermometers mounted at the base of the cold finger and at the end of the copper slab adjacent to the sample. These indicate a temperature increase on the order of 1–2 K between the cold finger and the sample. To achieve thermal contact at the lowest temperature a small amount of helium exchange gas is added to the sample chamber. Warming of the system is achieved using a 25 Ω heater mounted at the end of the cold finger. This produces a maximum heating rate of ~ 4 K/min and allows us to obtain spectra at any temperature between 10 K and room temperature.

To optimize the signal from the sample it is essential that it remains at the correct height relative to the focusing ellipsoidal mirrors. Because the cold finger cryostat contracts on cooling we must adjust the height of the cryostat before taking data at a different temperature. As shown in Fig. 1, this is achieved using a large spacer nut that supports the cryostat above the compression o-ring fitting. The plastic spacer has internal threads of 1 $\frac{3}{4}$ in. diameter at a pitch of 20 threads/in. This allows us to adjust the height of the sample to a precision of 0.1 mm per 28° of rotation. Control measurements indicate that the raising and lowering of the cryostat within the compression fitting do not cause any detectable pressure change in the vacuum chamber.

The adsorbate gas can be added to the system at any temperature above its boiling point. In the case of hydrogen, pressures in excess of an atmosphere are quite often required to achieve significant loading at room temperature. Our system had a maximum pressure rating of 100 bars. The loading pressure is measured using a pressure transducer with a rated accuracy of 0.5 bars. At lower temperature where such high pressures are no longer required, the adsorbate gas can be added to the system by first filling a calibrated volume (25 cm³) to a known pressure. This is determined using a low-pressure transducer with a rated accuracy of 1 mbar. The entire quantity of gas is then allowed into the sample chamber to adsorb onto the sample.

Loading of hydrogen within a C₆₀ powder is complicated by the fact that the kinetics for hydrogen diffusion within the C₆₀ lattice are extremely slow even at room temperature.⁸ Loading at temperatures significantly below ambient is practically unfeasible due to the excessive time scale. In our case using coarse powder with particle dimensions on the order of a millimeter it requires three days to achieve complete loading at room temperature. At this point the loading pressure could be removed and only a small fraction of the adsorbed hydrogen escaped from the sample during the 15 min required to reach base temperature.

IV. RESULTS AND DISCUSSION

Figure 3 shows the vibrational-rotational absorption spectrum for hydrogen molecules trapped within a C₆₀ lattice. The hydrogen is bound at an interstitial site with octahedral symmetry.⁹ It is known that this is the only type of site occupied and that the sites are well separated from each other

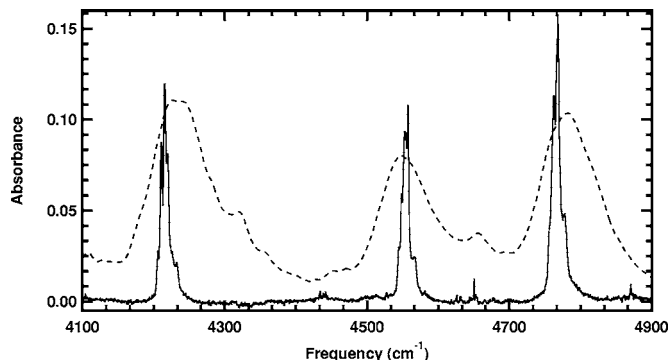


FIG. 3. Temperature dependence of the DRIFT spectra of the fundamental vibrational transition of H₂ in C₆₀. The absorbance at room temperature (dashed line) is scaled up by a factor of 3. The solid line shows the absorbance at 10 K. The prominent features are the translational-rotational transitions.

(10 Å) with, to a good approximation, only one hydrogen molecule per site.¹⁰ As such the system represents an ideal example of a molecule in a box. The detailed nature of the quantum dynamics of the trapped H₂ is the subject of another paper.¹¹ For now we present only a brief explanation of the absorption spectrum since our main purpose is to illustrate the significant advantages of obtaining a DRIFT spectrum at 10 K versus room temperature.

As a homonuclear diatomic molecule, H₂ has no intrinsic infrared activity. The observed absorption spectrum arises solely through the presence of dipole moments induced by interactions between hydrogen and host.⁴ Free hydrogen vibrates at a frequency of 4161 cm⁻¹ and in addition acts as a near perfect quantum rotor with rotational energy levels,

$$E(J) = B_v J(J+1), \quad (1)$$

where J is the rotational quantum number and B_v the rotational constant is 59 cm⁻¹ for H₂ in its ground vibrational state and 56 cm⁻¹ in its first excited vibrational state.¹² The selection rules for photon induced transitions are $\Delta J=0$ (Q transitions) and $\Delta J=\pm 2$ (S and O transitions).¹³ In addition infrared spectroscopy is sensitive to the localized translational modes of the trapped hydrogen's center of mass vibrating back and forth within the C₆₀ cavity. These modes are highly anharmonic and so at room temperature we observe a collection of broad overlapping peaks that cannot be resolved. The main room temperature absorption peaks shown in Fig. 3 have a full width at half maximum (FWHM) on the order of 70 cm⁻¹.

On cooling to 10 K the hydrogen molecules condense into their rotational and translational ground states. As shown in Fig. 3, the 10 K spectrum contains significantly sharper peaks with typical FWHM of 3 cm⁻¹ and some as narrow as 0.5 cm⁻¹. As a result of quantum statistics, constraining ortho-hydrogen with total nuclear spin of 1 to have odd values of J , three quarters of the hydrogen molecules remain in the $J=1$ rotational state even at 10 K. As such we expect to see four main absorption bands in our cold spectrum $Q(0):J=0 \rightarrow 0$, $Q(1):J=1 \rightarrow 1$, $S(0):J=0 \rightarrow 2$, and $S(1):J=1 \rightarrow 3$. Both Q transitions occur at quite similar frequencies in gas phase H₂ and so it is not surprising that they appear as a single feature in our absorption spectrum.

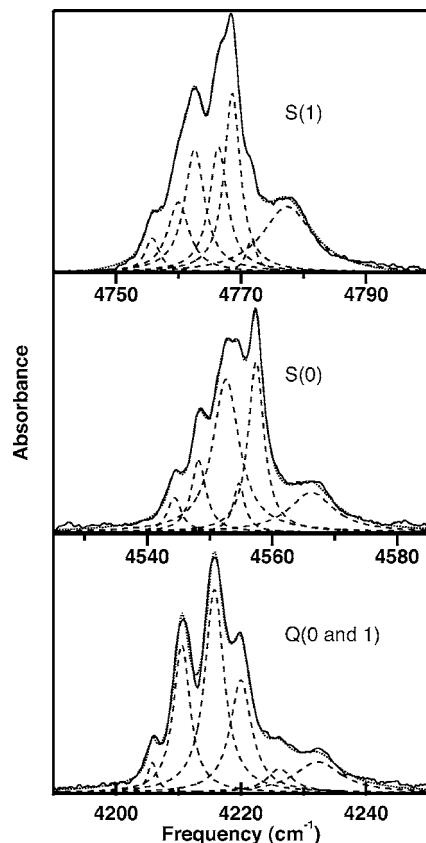


FIG. 4. Low-temperature DRIFT spectrum showing each of the main absorption bands of H_2 in C_{60} . The dashed curves show an empirical deconvolution of the data. The dotted curve represents the total fit. Spectra were obtained at 10 K with a 1 cm^{-1} resolution.

Figure 4 shows each of the main features on an expanded scale. It reveals that the bands are split into at least five peaks. These splittings are predicted to arise from crystal field effects and rotational-translational coupling.¹⁴ A simple deconvolution of the data reveals that Lorentzian line profiles produce a substantially better fit than Gaussian. This is

in agreement with the predictions of Herman and Lewis.¹⁵ From this we conclude that the widths are the result of lifetime broadening or dephasing effects rather than site inhomogeneity. The FWHMs are typically on the order of $3\text{--}4\text{ cm}^{-1}$ with in each case a much broader shoulder on the high frequency side. A more complete analysis of the frequency splitting, width, and intensity of the different peaks provides a wealth of information that can be used to map out the nature of the hydrogen host interaction potential.¹¹

ACKNOWLEDGMENTS

The authors acknowledge Bill Marton for his help with the construction of the vacuum housing used in this work. The authors also acknowledge the donors of the American Chemical Society Petroleum Research Fund and Research Corporation for their partial support of this research.

- ¹L. Schlapbach and A. Züttel, *Nature (London)* **414**, 353 (2001).
- ²M. S. Dresselhaus, G. W. Crabtree, and M. V. Buchanan, *MRS Bull.* **30**, 518 (2005).
- ³M. Fichtner, *Adv. Eng. Mater.* **7**, 443 (2005).
- ⁴H. E. Hallam, *Vibrational Spectroscopy of Trapped Species* (Wiley, New York, 1973).
- ⁵N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keefe, and O. M. Yaghi, *Science* **300**, 1127 (2003).
- ⁶W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy* (Interscience, New York, 1966).
- ⁷V. B. Kazansky, V. Yu. Borovkov, and H. G. Karge, *J. Chem. Soc., Faraday Trans.* **93**, 1843 (1997).
- ⁸S. A. FitzGerald, S. Forth, and M. Rinkoski, *Phys. Rev. B* **65**, 140302(R) (2002).
- 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).
- ¹⁰B. P. Uberuaga, A. F. Voter, K. K. Sieber, and D. S. Sholl, *Phys. Rev. Lett.* **91**, 15901 (2003).
- ¹¹S. A. FitzGerald, H. O. H. Churchill, P. M. Korngut, C. B. Simmons, and Y. E. Strangas, *Phys. Rev. B* **73**, 155409 (2006).
- ¹²S. S. Bragg, J. W. Brault, and W. H. Smith, *Astrophys. J.* **263**, 999 (1982).
- ¹³G. Herzberg, *Spectra of Diatomic Molecules* Molecular Spectra and Molecular Structure, Vol. 1 reprint ed. (Krieger, Malabar, Florida, 1989).
- ¹⁴T. Yildirim and A. B. Harris, *Phys. Rev. B* **66**, 214301 (2002).
- ¹⁵R. M. Herman and J. C. Lewis, *Phys. Rev. B* **73**, 155408 (2006).