Vibration–Rotation–Translation Spectrum of Molecular Hydrogen in Fullerite Lattices around 80 K

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(Dated: May 21, 2008)

Calculations are presented for the fundamental vibration–rotation spectrum of H₂ in fcc C₆₀ (fullerite) lattices near 80 K using the approach and the parameters used by Herman and Lewis¹,² at 293 K. Good agreement is found with recent DRIFT spectra of FitzGerald et al.³.

PACS numbers: 68.43.Pq, 78.30.Na, 33.20.Ea

I. INTRODUCTION

The vibration-rotation-translation spectrum of molecular hydrogen, H₂ trapped in C₆₀ (fullerite) lattices has been a subject of recent interest. Following the publication of the measurements by FitzGerald et al.⁴ of these spectra at room temperature through diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) the present authors¹,² have recently published a comprehensive theory for the spectra at 293 K. The theoretical spectra were quite well matched to the observed spectra with few free parameters, beginning with an exp −6 potential between H₂ and each C atom, summed over all C atoms in the surrounding six nearest neighbor C₆₀ molecules in the fcc fullerite lattice. The resulting C−H₂ interaction potential has a well depth of ε = 3.25 meV, and a characteristic radius (for which the interaction potential energy is zero) σ = 3.22 Å. In view of the good agreement between theory and observation achieved, it is important to test the theory in different situations, to see if the good agreement still holds. The present paper is an attempt to explain the more recently measured 80 K spectrum observed by FitzGerald³ by using the same theory and parameters, insofar as it is possible to do so, under the conditions of a lowered temperature. However, we have not attempted to fit the 10 K spectrum recently published by FitzGerald, Churchill, Korngut, Simmons and Strangas⁵.

In ref. (¹) the principal features of the 293 K spectrum were seen to arise from the H₂ molecules trapped in sites of octahedral symmetry, of which there are two per C₆₀ molecule in the fcc fullerite lattice. In these sites, it was discovered that the potential energy of translation of the H₂ molecule and the corresponding translational states are successfully approximated by a potential that is separable in the principal directions defined by the six nearest C₆₀ molecules. The induced transition dipoles occur as a result of displacements from the equilibrium octahedral symmetry sites as the H₂ molecules oscillate within the cavities provided by the surrounding C₆₀ molecules. The dipole operators therefore have opposite signs for opposite displacements, such that the important transitions are those for which the translational quantum number for motions parallel to a principal axis along which the incident light has a polarization component changes by ±1, with the quantum numbers for translational oscillation on the perpendicular axes remaining fixed. Thus, accompanying any particular vibration–rotation transition, there is a band of R–type translational transitions in which n± increases by unity, and a corresponding band of P–type transitions in which n± decreases by unity, for the z−polarized component of the electric field. In addition, weak features are observed for which there is no translational state change. According to ref. (¹) these arise from those H₂ molecules trapped in sites not having octahedral symmetry, such as surface pores or C₆₀ vacancy sites, which they can occupy with another H₂ molecule. The properties of the induced dipoles are presented in ref. (¹) and will remain the same in the present analysis. The changed parameters will be the equilibrium separation of the H₂ and C₆₀ molecules, due to thermal contraction of the fullerite lattice, and the temperature itself, which enters the assessment of occupation probabilities for the various rotation-translation energies and other statistical distributions utilized in the calculations as well as the relaxation parameters for the translational states and for the internal transitions by themselves. Finally, because the 80 K observations were made for sample geometries different from those used for the 293 K observations, the overall normalization of the spectrum may differ from that for the 293 K case previously analyzed, as well as the fractional number of H₂ molecules located in non–centrosymmetric sites.
Details of the apparatus and experimental methods used by FitzGerald et al. are to be found in refs. (4-8). The 80 K spectrum shown in Figs. 2 and 3 was taken later than that shown in Fig. 1 and is considered by FitzGerald3 to be a better representation of the H2 spectrum at 80 K than his earlier spectrum. Indeed, the experimental spectrum shown in Fig. 1 appears to be well-explained by the theoretical spectrum at 125 K, as noted below, suggesting that there may have been an inadvertent temperature increase associated with that measurement. 

For the observed spectrum in Fig. 1 the shoulders are resolved or almost resolved. For the $Q_1 (J)_P$ peak there is a shoulder corresponding to $n_z = 2 \rightarrow 1$. Finally, $Q_1 (J)_R$, $S_1 (0)_R$, and $S_1 (1)_R$ appear to have weak shoulders corresponding to $n_z = 2 \rightarrow 3$.

In analyzing such low temperature spectra, the following major aspects must be considered: 1) the three peak heights, relative to each other; 2) the magnitudes and positions of the smaller peaks associated with changes in translational state; 3) the line widths; and 4) the intensities of the “sharktooth” features.

For the $Q_1 (J)$ peak, both $J = 0 \rightarrow 0$ and $J = 1 \rightarrow 1$ transitions are involved, with the $B_{21}$ and $B_{23}$ induced dipole components contributing to the $1 \rightarrow 1$ transition while only the $B_{10}$ component contributes to the $0 \rightarrow 0$ transition. By contrast, the $S_1 (0)$ and $S_2 (1)$ lines involve transitions only from the $J = 0$ and $J = 1$ states respectively, and therefore the ratios of these peak intensities should provide a measure of rotational state occupation.

A difficulty appears to exist in this, however, in that with the 80 K spectrum it appears as if the peak of the tallest $S_1 (0)_R$ line may not be fully represented, possibly as an artifact of the Fourier transform process involved in constructing the DRIFT spectrum, so that the ratio of the tallest $S_1 (1)_R$ to the tallest $S_1 (0)_R$ peak may not be accurately deducible from the figure. Nevertheless, for the 80 K figure shown in Fig. 2 it is apparent that the ratio of peak heights as calculated at 80 K is clearly unacceptable. To improve this situation, it appears reasonable in the light of the comments in ref. (5) to suggest that the ortho–to–para conversion freezes out at a temperature substantially higher than 80 K, presumably because this conversion is activated as the H2 molecules occupy and traverse the tetrahedral lattice sites that are occupied in transient fashion in the diffusion of H2 into the fullerite lattice. But because of the high energy of H2 tetrahedral sites, this fails to be a possibility at lower temperatures. Accordingly, the ratio of H2 molecules in $J = 1$ rotational states to those in $J = 0$ states will be affected by this freezing-out, and its influence on the spectra will be noted below.

Ortho–para freezing at 200 K was also considered by FitzGerald.

From the positions and peak heights of all of the sharp peaks involving translational state changes it is clear that the translational energies associated with the 293 K case are too small to account for these spectra. This almost certainly reflects the thermal contraction of the fullerite lattice which takes place(8,10) in going to the lower temperature, with the H2–fullerene equilibrium distance decreasing by 0.2 a.u., or 1.5%, which is in rough agreement with the translational energy shifts are somewhat surprisingly large, as can be seen by comparing the transition energies shown in Table I. These energies have been established through the separation model and verified independently through exact DVR calculations.

The Lorentzian line widths of all transitions are expected to be proportional to temperature. The reasoning is as follows: the fullerite lattice undergoes slow oscillations with very high phonon occupation numbers, far from any quantum limit. Individual $C_{60}$ molecules can

II. THEORETICAL CONSIDERATIONS

By referring to the 80 K observed spectrum shown in Fig. 2 the following features can be identified (frequencies are given in cm$^{-1}$):

- $Q_1 (J)_P$: $J \rightarrow J$, $n_z = 1 \rightarrow 0$
- $Q_1 (J)_R$: “sharktooth” showing a static vibrational shift as per ref. (1).
- $Q_1 (J)_R$: for $n_z = 0 \rightarrow 1$
- $Q_1 (J)_R$: $n_z = 1 \rightarrow 2$
- $S_1 (0)_P$: $J = 0 \rightarrow 2$, $n_z = 1 \rightarrow 0$
- $S_1 (0)_R$: “sharktooth”.
- $S_1 (1)_P$: $J = 1 \rightarrow 3$
- $S_1 (0)_R$: $n_z = 0 \rightarrow 1$
- $S_1 (0)_R$: $n_z = 1 \rightarrow 2$
- $S_1 (1)_R$: “sharktooth”.
- $S_1 (1)_R$: $n_z = 0 \rightarrow 1$
- $S_1 (1)_R$: $n_z = 1 \rightarrow 2$

For the observed spectrum in Fig. 1 the shoulders referred to above are resolved or almost resolved. For the $Q_1 (J)_P$ peak there is a shoulder corresponding to $n_z = 2 \rightarrow 1$. Finally, $Q_1 (J)_R$, $S_1 (0)_R$, and $S_1 (1)_R$ appear to have weak shoulders corresponding to $n_z = 2 \rightarrow 3$.
therefore be thought of as undergoing classical motions under the influence of their neighbors, with kinetic energies being proportional to the temperature. Perturbations of the H$_2$ translational states might be proportional to the fluctuations in thermal energy of the surroundings, therefore, though the fluctuations themselves would be reduced in time as the velocity increases. Therefore a random fluctuation in phase for the translational state would vary as $\sqrt{T}$. Because line widths respond to the squares of phase shifts the overall dependence of the Lorentz line widths would therefore be expected to vary as $T$ itself.

The predicted linewidths at 80 K appear to be somewhat smaller than observed, as can be seen in Fig. 2. For this reason we feel that an operating temperature around 90 K may well be the case for the nominally 80 K observation. Obviously these arguments are somewhat qualitative, and a more quantitative analysis would eventually be desirable. However, in view of the rather good agreement between theory and observation seen in the Fig. 3, this would seem to be a good assumption.

Finally, the sharktooth peaks depend on the relative number of H$_2$ molecules found in non-centrosymmetric sites. This fraction can change according to the preparation of the sample and other details of the experimental procedures. In particular, samples with larger C$_{60}$ crystallites were used at the lower temperatures, so that a lower fraction of such sites would be anticipated. The present calculations are carried out with this fraction being reduced by a factor of five compared with the calculations at 293 K.

**III. RESULTS AND DISCUSSION**

The theoretical analysis in the present work is identical to that used for the 293 K spectrum, with the above changes noted. In view of the large differences in the two spectra, as shown in Fig. 1 as against Figs. 2 and 3, taken at different times under different circumstances, and with the uncertainty in thermalization of the samples to the 80 K bath with the radiation providing heat to the samples, our conclusion is that the curve shown in Fig. 1 was characterized by a temperature of approximately 125 K. The theoretical curve with which the spectrum is compared was computed for the temperature 125 K, with the resulting agreement being good.

In Fig. 2, we show the spectrum taken at what we regard as a true temperature much closer to 80 K. The sharp peak heights obviously are not well represented by the theory at 80 K, and the lines in the theoretical spectrum appear to be too narrow. Also, the $Q_P$ and $S(1)_R$ ($n_z = 1 \rightarrow 2$) features are too weak at 80 K.

We therefore assume that the temperature of the sample for the second DRIFTS was closer to 90 K than to 80 K, with ortho-para ratio which would be characteristic of an equilibrium situation at 125 K. The resulting curve for $T = 90$ K and ortho-para ratio characteristic of 125 K, shown in Fig. 3, is the best that we have been able to achieve, though differences from the experimental curve are apparent. As mentioned above, the small peaks are in some cases not well represented, and the major peak heights (particularly the magnitude of the $Q_1(J)$
tall peak relative to the remainder of the spectrum) still show significant discrepancies.

We have also calculated the theoretical spectrum for 90 K with ortho–para conversion characteristic of 200 K. It is very similar to the spectrum at 90 K with ortho–para ratio at 125 K shown in Fig. 3. Freezing at 125 K gives slightly better agreement with the observed spectrum around 4550 cm$^{-1}$ though not quite so good agreement in the 4780 – 4800 cm$^{-1}$ region. Freezing at 200 K gives worse agreement around 4550 cm$^{-1}$ but better agreement around 4780 – 4800 cm$^{-1}$: the population of the $J = 0$ state is too small at that temperature for good agreement.

Acknowledgments

We thank S. A. FitzGerald for providing us with his DRIFTS data in Figs. 1, 2, and 3, and for several extensive and thorough discussions of relevant theory and experimentation.

One of us (RMH) acknowledges useful discussions on ortho–para conversion of H$_2$ with M. J. Stavola and W. B. Fowler.

We acknowledge useful discussions on graphene and carbon nanostructures with M. W. Cole, P. C. Eklund, and V. Crespi.

One of us (JCL) acknowledges support from the Natural Sciences and Engineering Research Council of Canada, and thanks the Department of Physics of the Pennsylvania State University for its hospitality.