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Author(s)	Kohama, Yoshimitsu; Rachi, Takeshi; Jing, Ju; Li, Zhaofei; Tang, Jun; Kumashiro, Ryotaro; Izumisawa, Satoru; Kawaji, Hitoshi; Atake, Tooru; Sawa, Hiroshi; Murata, Yasujiro; Komatsu, Koichi; Tanigaki, Katsumi
Citation	PHYSICAL REVIEW LETTERS (2009), 103(7)
Issue Date	2009-08
URL	http://hdl.handle.net/2433/109858
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Type	Journal Article
Textversion	publisher

Rotational Sublevels of an Ortho-Hydrogen Molecule Encapsulated in an Isotropic C₆₀ Cage

Yoshimitsu Kohama,^{1,*} Takeshi Rachi,² Ju Jing,² Zhaofei Li,² Jun Tang,² Ryotaro Kumashiro,² Satoru Izumisawa,¹ Hitoshi Kawaji,¹ Tooru Atake,¹ Hiroshi Sawa,³ Yasujiro Murata,⁴ Koichi Komatsu,⁵ and Katsumi Tanigaki^{2,†}

¹Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8503 Japan

²Department of Physics, Tohoku University, 6-3 Aoba Aramaki Aoba-ku, Sendai, 980-8578, Japan

³Department of Applied Physics, Nagoya University, Furo-cho, Chidane-ku, Nagoya, 464-8603, Japan

⁴Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

⁵Fukui University of Technology, Gakuen, Fukui 910-8505, Japan

(Received 24 February 2009; published 12 August 2009)

From specific heat measurements in high quality H₂@C₆₀ samples performed over a broad temperature range, we obtain the smallest yet observed splitting of rotational energy sublevels of encapsulated single H₂ molecules, 0.1–0.2 meV, in the nearly spherical potential well provided by highly isotropic C₆₀ cages. Additionally, we find evidence of the quantized oscillation state of isolated H₂ in the C₆₀ cage. The minuscule splitting indicates that H₂@C₆₀ provides unprecedented opportunities to study free-molecule quantum dynamic properties.

DOI: 10.1103/PhysRevLett.103.073001

PACS numbers: 33.20.Sn, 33.20.Tp, 61.48.–c, 65.40.Ba

Molecular hydrogen (H₂), the simplest system among all molecules, has been studied extensively to date [1–3], and its electronic spectra have been fundamental in establishing the fundamentals of quantum mechanics. An H₂ molecule is not expected to be completely localized at lattice sites even in the solid state at 0 K due to its large zero point motion. H₂ retains translational freedom as a translational quantum solid [1]. The rotational motion of the H₂ molecule also persists, and thus an H₂ crystal is also an orientational quantum solid [1]. The unique free-rotor description is a result of the nuclear spin isomers denoted by para-H₂ $J = 0, 2, 4$ and ortho-H₂ $J = 1, 3, 5, \dots$, where J is the rotational quantum number. Because of wave-function symmetry requirements, the conversion between these spin isomers is forbidden, and, therefore, the energetically higher $J = 1$ state remains an angular momentum degree of freedom down to 0 K. Indeed, the rotational motion in solid H₂ can be described as a nearly three-dimensional free rotor where the rotational motion is barely disturbed by the neighboring hydrogen molecules. The small interaction originating from the neighboring molecules is still a central issue in the experimental research of solid H₂ because these interactions can drastically modify the ortho-para conversion, crystal structure, and rotational and translational spectra [1].

Fullerene encapsulated H₂ molecules (H₂@C₆₀) have been only recently macroscopically synthesized by organic reactions known as the “molecular surgery method” [4] and offer an unprecedented opportunity to study the rotational and translational states of the H₂ molecule. The molecular dynamics of endohedral H₂ have recently been studied by nuclear magnetic resonance [5] and inelastic neutron scattering measurements [6] by means of H₂@ATOCF (ATOCF: azacyclic-thiacyclic molecule, an open cage structure of C₆₀). The results, however, indicate that the endohedral H₂ in H₂@ATOCF shows limited 3D

rotational freedom due to the low symmetry of open cage C₆₀. Although infrared spectroscopy was recently used to evaluate the rotational-vibrational coupling [7], this technique is not sensitive enough to detect the fine structure of the $J = 1$ triply degenerate rotational sublevels [8,9] that can provide direct information about the intriguing rotational states. In this Letter, we discuss the first specific heat results of 99% pure H₂@C₆₀ from room temperature down to 0.085 K. An anomaly observed at $T = 0.6$ K is attributed to the almost degenerate quantized rotational level state. The observed small 0.1–0.2 meV energy splitting between states allows us to conclude that the encapsulated H₂ in the C₆₀ cage can be regarded as an almost 3D free quantum rotor.

H₂@C₆₀ was synthesized by organic chemical reactions by opening and closing the C₆₀ cage structure as described elsewhere [4]. Repeated column chromatography isolation was used to produce 99% pure H₂@C₆₀. In order to increase crystallinity of the H₂@C₆₀ powder, the samples were repeatedly dissolved in toluene and recrystallized on a surface of a glass plate while keeping the plate temperature at ~ 400 K.

High resolution x-ray powder diffraction data were collected at different temperatures in the BL02B2 beam line ($\lambda = 1.0000$ Å) at SPring-8, followed by maximum entropy method (MEM)-Rietveld refinement to analyze the crystallographic structure of the samples. Specific heat measurements were made using a thermal relaxation time method with two calorimeters for different temperature regions. From 0.085 to 5 K, a homemade calorimeter in a ³He/⁴He dilution refrigerator was used. To obtain good thermal contact, the specimen was pressed between two plates of sapphire together with a small amount of Apiezon-N grease. The heat capacity of the sample was obtained by subtracting the contribution of the sapphire, Apiezon-N grease, and the sample cell from the total heat

capacity. The heat capacity of the sapphire plates was extremely small, and the contribution was estimated by the Debye T^3 extrapolation from the data for sapphire reference standard material (NIST SRM 720). From 2 to 300 K, the specific heat was measured using a physical property measurement system (PPMS) from Quantum Design. The values of specific heat of $H_2@C_{60}$ obtained by the two calorimeters agree in the overlapping temperature region from 2 to 5 K.

Both C_{60} and $H_2@C_{60}$ crystals adopt a primitive cubic $Pa\bar{3}$ symmetry having two orientational orderings at low temperatures [10]. On the basis of the intensity of the (200) peak, where the form factor of C_{60} and endohedral H_2 can cancel each other, it can be concluded that an H_2 molecule was encapsulated at the center inside the cage. The density maps illustrated in Fig. 1, obtained using MEM-Rietveld analyses for both C_{60} and $H_2@C_{60}$, show H_2 in the center of the C_{60} cage.

C_p data for $H_2@C_{60}$ and C_{60} (with the same treatment for comparison) are shown as a function of temperature in Fig. 2. Two distinct anomalies were observed: one being around 260 K and the other around 0.6 K. The former transition (260 K) is the well known rotational disorder (high- T , space group $Fm\bar{3}m$) to rotational order (low- T , space group $Pa\bar{3}$) phase transition of C_{60} [10,11]. In the high-temperature regime, the C_{60} rotational barrier is smaller than the thermal energy $k_B T$, and C_{60} freely rotates, whereas the intermolecular interactions of hexagon-hexagon and hexagon-pentagon fusion block the C_{60} rotation leading to its lower symmetry with two preferred orientations in the low-temperature regime [10]. The same rotational phase transition temperature for both $H_2@C_{60}$ and C_{60} implies that the rotational motion of the C_{60} cage is not affected by the endohedral H_2 molecule.

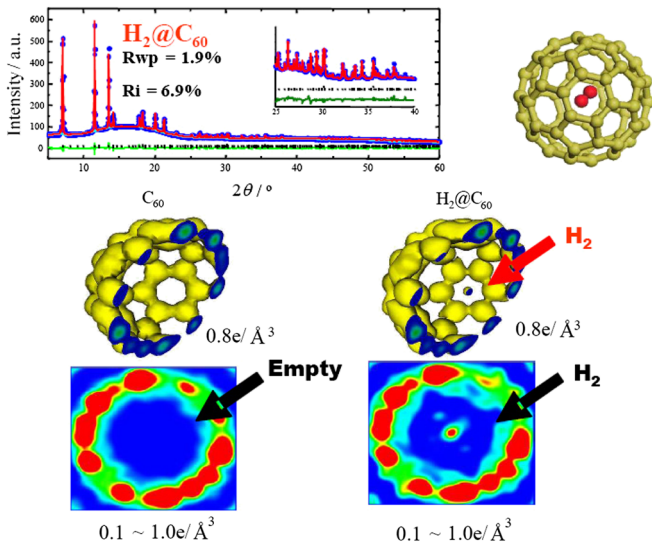


FIG. 1 (color online). X-ray diffraction pattern and electron density surface of $H_2@C_{60}$. The view (right side) shows that an endohedral H_2 molecule locates in the center of the cage.

In Fig. 2, it is possible to see that C_p for $H_2@C_{60}$ is larger than that for pure C_{60} over the entire temperature range. Given that the crystal structure of $H_2@C_{60}$ is the same as that of C_{60} , it is reasonable to assume that the contribution from the C_{60} cage to the specific heat is identical for both compounds. Therefore, the difference in C_p (ΔC_p ; excess specific heat obtained by subtracting the C_p of C_{60} from that of $H_2@C_{60}$) shown in Fig. 3 is ascribed to endohedral H_2 . Since H_2 is a diatomic molecule, there are 6 degrees of freedom for H_2 : i.e., 3 translational (C_{trans}), 2 rotational (C_{rot}), and 1 intramolecular vibrational (C_{vib}) degrees of freedom. Considering that the H_2 intramolecular stretching vibration frequency of 4161 cm^{-1} [1] is too high to be excited below room temperature, the excess ΔC_p likely originates from C_{trans} and C_{rot} , i.e., $\Delta C_p \approx C_{trans} + C_{rot}$.

The rotational specific heat C_{rot} is affected by the presence of ortho-para conversion. Indeed, in the presence of such conversion, C_{rot} is calculated as $C_{rot} = d/dT\{RT^2 d/dT[\ln(0.25Z_{para} + 0.75Z_{ortho})]\}$ while, in the absence of the ortho-para conversion, C_{rot} is given by $C_{rot} = 0.25d/dT\{RT^2 d/dT[\ln(Z_{para})]\} + 0.75d/dT\{RT^2 d/dT[\ln(Z_{ortho})]\}$, where the participation functions Z_{para} and Z_{ortho} are $Z = \sum (2J+1) \exp(-E_J/k_B T)$ and the rotational quantized energy levels are $E_J = B_J J(J+1)$ [5]. If the ortho-para conversion occurs, the equilibrium specific heat (C_{rot}^*) must show a large anomaly around 50 K as shown in Fig. 3 [12] according to the equation given earlier. In the present experiments, however, no such anomaly was observed, and therefore our results indicate that the ortho-para conversion is prohibited in $H_2@C_{60}$. Similar conclusions are reported in the open cage system $H_2@ATOCF$ [5,6].

The translational motion of H_2 corresponds to the oscillation of the center of mass, bound by the spherical potential created by the C_{60} framework. Similar oscillation of endohedral intercalants has been observed in other sys-

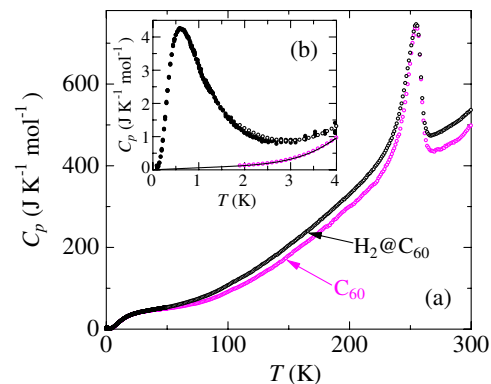


FIG. 2 (color online). Specific heat of C_{60} and $H_2@C_{60}$. (a) Open circles are measured by a PPMS, and solid black circles are measured by a homemade calorimeter. The solid line was obtained by extrapolation.

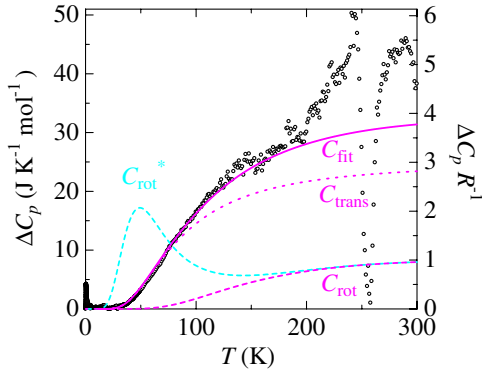


FIG. 3 (color online). Excess specific heat ΔC_p . These data (black circles) were obtained by subtracting the C_p data of C_{60} from that of $H_2@C_{60}$. For the calculation below 2 K, C_p of C_{60} is estimated by extrapolation to 0 K from temperatures above 2 K [shown in Fig. 2(b)]. The magenta solid curve indicates the fitted specific heat C_{fit} , which is the summation of C_{trans} (magenta dotted curve) and C_{rot} (magenta dashed curve), while the dashed cyan curve is the rotational C_p of H_2 with the equilibrium ortho-para ratio.

tems, such as clathrates and filled skutterudites, where the translational specific heat originating from the endohedral atoms is described accurately by the Einstein model [13,14]. In order to evaluate the translational energy of the endohedral H_2 molecule, we have also employed the Einstein model derived from the quantized energy levels of a harmonic oscillator, with an Einstein temperature Θ_E . This view is consistent with previous theoretical predictions [8,9] as well as the electron density map of H_2 described earlier. Applying these models with one fitting parameter Θ_E , we have calculated $C_{\text{fit}} = C_{\text{trans}} + C_{\text{rot}}$ in Fig. 3. As seen in Fig. 3, the curve fitted with $\Theta_E = 260$ K is in good agreement with the experimental data. We note that the deviation observed above 200 K is due to the orientational phase transition of C_{60} , which strongly depends on the crystal quality. Our analysis shows that the endohedral hydrogen molecule in $H_2@C_{60}$ can be described as an almost isolated harmonic oscillator with quantized translational motion confined in the C_{60} framework and acts as a free rotor without ortho-para conversion.

The translational energy can also be discussed by solving the Schrödinger equation for a single particle confined in an ideal three-dimensional spherical potential: $E_{\text{trans}}(n, \ell) = \beta_{n,\ell}^2 \hbar^2 / (2\mu r^2)$, where r is the radius of the cavity, $\beta_{n,\ell}$ is the n th root of the spherical Bessel function with the quantum numbers of n and ℓ , and μ is the reduced mass [5,6]. The translational energy difference between the ground and the first excited translation levels can thus be estimated from $\Delta_{\text{trans}} = E_{\text{trans}}(1, 1) - E_{\text{trans}}(1, 0) = 10.32\hbar^2 / (2\mu r^2)$ to be ~ 25 meV ($\Delta_{\text{trans}}/k_B \sim 290$ K) with $r = 0.65$ Å estimated from the diameter of the fullerene (7.1 Å) and the van der Waals radii of H (1.2 Å) and C (1.7 Å) [5]. The Θ_E used to fit ΔC_p is fairly consistent

with this translational energy and slightly larger than the translational energy of H_2 (~ 17.5 meV = 200 K [Ref. [6]]) in anisotropic open cage fullerenes. Considering that the Δ_{trans} is reduced by the increase of r , this difference can originate from the larger diameter along the two long axes of the open cage fullerene (7.3–7.8 Å) as compared to the isotropic C_{60} fullerene.

In the low-temperature region, a Schottky-like anomaly is clearly evident in Figs. 2 and 4. The entropy associated to this anomaly was calculated to be 6.8 $\text{J K}^{-1} \text{mol}^{-1}$ and displayed also in Fig. 4(b). Since the rotational excited levels in both ortho and para spin isomers are located a few hundred Kelvin above the ground state as discussed earlier [1,5,6], we take into consideration only the lowest rotational sublevels of the nuclear spin isomers ($J = 0$ for para- H_2 and $J = 1$ for ortho- H_2). The threefold degeneracy in the $J = 1$ level can be lifted by the energy potential in the low-temperature $Pa\bar{3}$ phase [15,16], and such splitting is expected to produce a C_p anomaly as the one observed in our experiment. Indeed, the expected excess entropy due to the splitting of the $J = 1$ level with 75% ortho- H_2 ($0.75R \ln 3 = 6.85$ $\text{J K}^{-1} \text{mol}^{-1}$) is quite close to the measured entropy. The ortho- H_2 fraction of 0.75, expected to hold in the entire temperature range [1,12], provides additional support for a forbidden ortho-para conversion in C_{60} cages. Additionally, we checked the sample dependence of the entropy and found it to be proportional to the H_2 content. This fact unambiguously supports the interpretation of the anomaly in terms of rotational sublevel splitting.

We have then tentatively analyzed the rotational sublevel splitting ΔE_{rot} of the triply degenerate $J = 1$ levels by employing a two-level Schottky model (one ground state and doubly degenerate excited states) which can be ex-

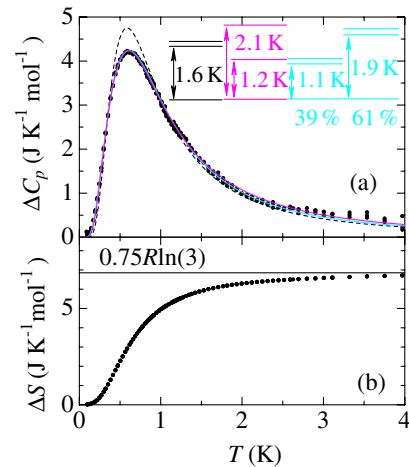


FIG. 4 (color online). Excess specific heat ΔC_p and excess entropy ΔS below 4 K. (a) The black dashed, magenta, and cyan curves indicate the results of two-level, three-level, and dual two-level Schottky fits, respectively. (b) ΔS was calculated from ΔC_p .

pected in the S_6 symmetry of a C_{60} molecule in the $Pa\bar{3}$ phase [15,16]. The best fit was achieved for $\Delta E_{\text{rot}} = 0.14$ meV ($\Delta E_{\text{rot}}/k_B = 1.6$ K) as shown in Fig. 4(a). Because a small disagreement remained as seen in the dashed line of Fig. 4(a), this encouraged us to apply a three-level model. A much better fit was achieved for $\Delta E_{\text{rot}} = 0.10$ ($\Delta E_{\text{rot}}/k_B = 1.2$ K) and 0.18 meV ($\Delta E_{\text{rot}}/k_B = 2.1$ K) as displayed in Fig. 4(a). The further splitting of the $J = 1$ level suggests that the local symmetry is slightly lower than S_6 symmetry. In fact, in the case of anisotropic $H_2@ATOCF$, a clear three-level splitting was observed ($\Delta E_{\text{rot}} = 1.50$ and 2.85 meV [6]). The magnitude of the splitting first elucidated in the present specific heat measurements shows rotational sublevel splitting much smaller than those of H_2 in the open caged fullerene [6] and of similar order to those of those observed in solid H_2 [1,17]. The large splitting of the rotational degeneracy observed in the open cage C_{60} is most likely caused by the anisotropic energy surface accommodating the H_2 molecule, and the rotational angular momentum of the ortho- H_2 is quenched. In contrast, the $J = 1$ rotational sublevel splitting is rather small in the higher symmetry of C_{60} , which allows one to treat the rotational spectrum as that of a 3D free quantum rotor.

A similarly good fit can be obtained when two types of rotational sublevel splitting in the scheme of one ground and two excited levels are used at the same time. This situation might become possible when the two types of orientation of C_{60} below 90 K are taken into consideration [10], because these orientations can lead to two different crystal fields within the $Pa\bar{3}$ space group depending on the orientations of C_{60} . The best fit was achieved for $\Delta E_{\text{rot}} = 0.095$ ($\Delta E_{\text{rot}}/k_B = 1.1$ K) and 0.16 meV ($\Delta E_{\text{rot}}/k_B = 1.9$ K) with fractions of 0.39 and 0.61. However, these values are far from the reported fractions of 0.165 and 0.835 [10]. An alternative possibility for explaining the small deviation from the simple two-level Schottky model is that another type of disorder induces a continuous distribution of crystal field effects. However, in our measurements, the shape of the low-temperature anomaly does not depend on the sample quality, which suggests that rotational sublevel distribution is not caused by such a disorder.

In summary, our low-temperature specific heat measurements provide the first experimental evidence for a small energy splitting of 0.1–0.2 meV in the $J = 1$ state of the ortho- H_2 nuclear spin isomer. This tiny rotational sublevel splitting is likely due to C_{60} having slightly less local symmetry than S_6 in the low-temperature $Pa\bar{3}$ phase. Our detailed analysis of the excess specific heat in the intermediate energy scale suggests that the confined H_2 molecule can be described as a quantized oscillator in a cage. A

single molecule or an atom endohedrally accommodated in C_{60} can be used as an ideal model compound for studying quantum dynamics, which cannot be realized in any conventional solid.

This work was supported by Grants-in-Aid (No. 18204030, No. 19014001, No. 18651075, and No. 18204032) and Scientific Research on Priority Areas (“New Materials Science Using Regulated Nano Spaces-Strategy in Ubiquitous Elements”) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Synchrotron radiation experiments were performed with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) as a Nanotechnology Support Project. This work was partially supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) (No. P07025 and No. 199728). The research was also partially supported by Tohoku University GCOE program. The authors thank Scott A. Baily and Marcelo Jaime for insightful discussions.

*To whom all correspondence should be addressed.

tanigaki@sspns.phys.tohoku.ac.jp

†ykohama@lanl.gov

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