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These samples are stable under ambient conditions. On is removed within a few minutes. It is spectroscopically when put into vacuum at a temperature of 200 °C all CO solid equivalent to that of CO gas at 5 MPa pressure. of CO : C_{60} are obtained, resulting in CO densities in these conditions samples with an almost 200 °C and a pressure of 10 MPa for about a day. Under C_{60} powder (Hoechst, "Super Gold Grade" C_{60}, purity >99.9%) or a thin film of C_{60} to CO at a temperature of 500-2250 cm\(^{-1}\) region is shown for four different temperatures. The spectral features due to C_{60} (not shown) are hardly influenced both in position and in intensity by the presence of CO. Only a slight frequency shift, up to 0.5 cm\(^{-1}\), is observed for some C_{60} modes.

Solid C_{60} can be intercalated with CO gas in a 1:1 ratio. The rovibrational motion of CO in these samples is studied as a function of temperature by IR and NMR spectroscopy. The observed spectra indicate a gradual transition from nearly free motion of CO at room temperature to hindered motion at low temperature, with only tunneling between symmetry equivalent orientations remaining. The observations are augmented by theory, and details on the local environment of the CO molecules are extracted. [S0031-9007(97)03839-8]

PACS numbers: 81.05.Tp, 31.70.Ks, 36.20.Ng, 76.60.-k

Rovibrational Motion of CO in Solid C_{60}


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Solid C_{60} can be intercalated with CO gas in a 1:1 ratio. The rovibrational motion of CO in these samples is studied as a function of temperature by IR and NMR spectroscopy. The observed spectra indicate a gradual transition from nearly free motion of CO at room temperature to hindered motion at low temperature, with only tunneling between symmetry equivalent orientations remaining. The observations are augmented by theory, and details on the local environment of the CO molecules are extracted. [S0031-9007(97)03839-8]

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For IR absorption experiments, 5 µm thick films of CO intercalated C_{60} on IR transparent substrates are used. Absorption spectra covering the 400-4000 cm\(^{-1}\) region are measured as a function of temperature with an experimental spectral resolution of 0.1 cm\(^{-1}\). Reference spectra are measured on the C_{60} films prior to their exposure to CO. After intercalation with CO, a new spectral structure that is strongly temperature dependent is readily identified. In Fig. 1(b) the additional structure appearing in the 2000-2250 cm\(^{-1}\) region is shown for four different temperatures. The spectral features due to C_{60} (not shown) are hardly influenced both in position and in intensity by the presence of CO. Only a slight frequency shift, up to 0.5 cm\(^{-1}\), is observed for some C_{60} modes.

For comparison, a spectrum of free CO molecules in the gas phase is shown in Fig. 1(a) while a spectrum of CO in an Ar matrix, where its rotational motion is completely blocked, is shown in Fig. 1(c). For CO in solid C_{60}, the broad spectral structure visible at room temperature gradually merges into a sharp resonance centered around 2124 cm\(^{-1}\) upon lowering the temperature. This resonance splits into at least two components upon approaching 0.6 K. The total integrated intensity of the CO related absorption is constant within a factor of 2 over the complete temperature range. There is no discontinuity in the appearance of the spectral structure associated with CO in crossing the rotational ordering sc \(\rightarrow\) fcc phase transition of C_{60} [2]. The simultaneously measured C_{60} spectra change discontinuously in crossing this phase transition, bracketed between 230-260 K (pure C_{60}: 260 K [9]), in full accord with observations reported by others for pristine C_{60} [10].

The series of spectra shown in Fig. 1(b) indicates a transition from a situation in which the CO molecules have significant freedom to move to a situation in which this motion is strongly hindered. At high temperature the wings of the spectra resemble the envelope of the rotational structure of a free CO molecule. The center peak confirmed that free CO molecules and pristine C_{60} are retrieved by the latter procedure.

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The weak structure appearing in the spectra about 2080 and 2190 cm\(^{-1}\) is caused by rather strong IR absorption bands that are intrinsic to C\(_\text{W}\) and that are not completely corrected for by subtracting the reference spectra. At 0.6 K the resonance is split into two components at 2123.3 and 2124.1 cm\(^{-1}\) with a full width at half maximum of 0.35 cm\(^{-1}\). In the lower trace of the inset the difference between the spectra recorded at 0.6 and 3.7 K is shown.

The line shape of the \(^{13}\)CO resonance from a static sample is strongly temperature dependent in this region, as shown in Fig. 2. At all temperatures shown, the width of the resonance is much smaller than the width of the chemical shift tensor of solid CO (\(\delta_\perp - \delta_\parallel \approx 365 \pm 20\) ppm at 4.2 K [13]). At room temperature, a symmetric line centered around the isotropic chemical shift value is found. This is in agreement with the expectation of the rapid motion of CO on the NMR time scale in an environment with \(O_h\) symmetry, which averages the second-rank tensor of the chemical shift anisotropy to its isotropic value. At temperatures below that of the sc \(\rightarrow\) fcc orientational ordering phase transition of C\(_{60}\), the symmetry of the “octahedral” site is reduced to \(S_4\). This lowering of the symmetry leads to a non-vanishing anisotropic contribution to the chemical shielding that is clearly reflected in the NMR line shape below 240 K. The experimental line shape at 200 K is described approximately by an axially symmetric chemical shift.
The quantum mechanical method to compute the energy levels of CO inside this cavity is based on a discrete variable representation for the radial coordinate of the CO center of mass and an expansion of the angular wave functions in symmetry adapted and coupled spherical harmonics [6]. The five-dimensional (5D) bound states for a rigid CO molecule inside this potential are calculated; three of the dimensions refer to the motion of the center of mass of CO, while the other two dimensions describe the orientation of the CO axis.

A three-dimensional (3D) equipotential surface for the position of the center of mass of CO with all C₆₀ molecules in the major orientation, obtained by taking a cut through the five-dimensional potential surface for an optimized CO orientation, is shown in Fig. 3. There are eight minima present in the potential for the position of the CO center of mass, all being off-center. In these minima the CO points with the oxygen atom in between three C₆₀ molecules towards the second nearest neighbors. The two equivalent (local) minima on the C₃-symmetry axis are approximately 30 cm⁻¹ less deep than the six equivalent (global) minima along the three other cube diagonals. In contrast, with all C₆₀ molecules in the minor orientation, the calculation predicts the minima on the C₃ axis to be the global minima. If we assume that in the 200–230 K range the C₆₀ molecules rapidly interconvert between the major and the minor orientation, an effective potential that is a linear combination of the ones just described, and that still has $S_6$ symmetry, is sampled by the NMR measurements. In a simple model, the orientational distribution for the CO molecules described above may be replaced by the eight discrete minima. Then, the motionally averaged chemical shielding tensor [14] is the weighted sum of eight axially symmetric second-rank tensors, of which six and two, respectively, are symmetry equivalent. The principal values of all tensors may be assumed to be identical (supported by the appearance of a single CO resonance in the MAS spectrum) but the principal axes differ. A preferential population of the six equivalent minima leads to an averaged chemical shift tensor with an inverted sign of the asymmetry ($\delta_\perp - \delta_\parallel$) with respect to the original tensor.

In Fig. 4 the observed IR spectrum of CO in solid C₆₀ measured at 203 K is compared to the calculated IR spectrum. The calculation is done in $S_6$ symmetry, with all C₆₀ molecules in the major orientation. For a true comparison with the experimental spectrum, a superposition of calculated spectra belonging to that of CO in sites with C₆₀ molecules in random orientations has to be made. This will lead to a blurring of the sharp spectral structures in the calculated spectrum, bringing this in even better agreement with experiment.

Below liquid nitrogen temperature, the major and minor orientations of C₆₀ are randomly frozen throughout the solid in a 5:1 ratio [15]. Under the assumption that this ratio is the same for C₆₀ intercalated with CO, this leaves approximately one-third of the CO molecules surrounded solely by C₆₀ molecules in the major orientation. These CO molecules are in a potential with six equivalent global minima, with a calculated tunnel splitting on the order of a cm⁻¹. In the IR spectrum this will result in two almost equally strong components separated by twice the tunnel splitting. The extra intensity in the high-frequency
component in the 0.6 K IR spectrum is attributed to the other two-thirds of the CO molecules that are in sites in which no measurable tunnel splitting is expected. The observed splitting of almost 1 cm$^{-1}$ in the IR spectrum at low temperature is interpreted as the direct spectroscopic signature of quantum-mechanical tunneling motion of the CO molecule. This interpretation is substantiated by the observed intensity transfer from the low-frequency component to the high-frequency component in reducing the temperature from 3.7 K to 0.6 K, as shown in the difference spectrum in the inset of Fig. 1(b).

Small molecules inside fullerene cages have been suggested to form an ideal system for the study of nearly free molecular rotation in the solid, and experimental evidence for the motion of a scandium trimer inside a C$_{82}$ fullerene cage has, for instance, been reported [16]. In addition, it has been pointed out that small polar molecules trapped inside the highly symmetric C$_{60}$ cage might be considered the building blocks for an ideal electric dipolar lattice [17]. The results reported here indicate that samples in which small molecules are trapped in the octahedral sites of solid C$_{60}$, i.e., in between C$_{60}$ molecules, samples that are much easier to produce, are equally interesting and promising and might show many of the characteristics, and enable many of the applications, anticipated for the corresponding endohedral species. In addition, it is demonstrated that molecules such as CO intercalated in fullerene samples are a very sensitive local probe of crystal structure and molecular orientation. It has also been shown here that gases can be efficiently stored in solid fullerene samples. The understanding of the guest-host interaction in a well-defined system as described here is a prerequisite for the understanding of gas storage in more complicated fullerene-related solids as, for instance, the recently reported storage of hydrogen in carbon nanotube material [18].

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[13] A. A. Gibson, T. A. Scott, and E. Fukushima, J. Magn. Res. 27, 29 (1977). Note that in this publication the chemical shift scale is reversed compared to our Fig. 2.