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Dynamics of CO Molecules in Solid C₆₀ as a Function of Cavity Size

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The rovibrational motion of CO intercalated in the octahedral site of solid C₆₀ is monitored as a function of pressure via infrared (IR) absorption spectroscopy. The increased hindering of the motion of the CO molecule, when the pressure is tuned from ambient to 32 kbar, is reflected in a dramatic change in the observed IR spectra. A large part of the transition from translationally and rotationally free molecules in a box to rigidly oriented molecules can thus be studied experimentally, and accurately described theoretically. [S0031-9007(98)06254-1]

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An intriguing possibility offered by the fullerenes, as already remarked by Kroto *et al.* in 1985 [1], is to experimentally study the dynamics of nearly free atoms and molecules confined to the inside of the carbon cages [2]. Soon after a production method for macroscopic amounts of fullerenes was developed and first details about the structure of solid C₆₀ became available, it was demonstrated that the sites *in between* the C₆₀ spheres in the solid are equally well suited for holding atoms and small molecules [3]. Recently, we have demonstrated that CO molecules can be efficiently squeezed into the octahedral sites of solid C₆₀, and we have studied the dynamics of CO in the interstitial sites using infrared (IR) absorption and ¹³C nuclear magnetic resonance (NMR) spectroscopy [4]. Under ambient conditions, the dynamics of CO in solid C₆₀ is observed to be the dynamics of a “stick” in a rigid square box with walls that are curved inward, which as such is an example of a classically chaotic system [5].

A unique possibility offered by the intercalated samples is to experimentally modify the size of the box in which the guest molecule is moving by applying hydrostatic pressure. From x-ray analysis of pristine C₆₀ it is known that, if put under pressure, the C₆₀ molecules themselves are not significantly compressed, but merely move closer together against the relatively weak intermolecular van der Waals forces [6,7]. A moderate pressure of 32 kbar already leads to a reduction in the diameter of the sphere that can be enclosed in the octahedral site by 15% [7]. For CO molecules in the site formed by the surrounding C₆₀ molecules, this yields the possibility to dramatically influence the dynamics by decreasing the size of the box, and to study the transition from classically chaotic motion to harmonic librational motion around equilibrium orientations.

In this Letter we report on the influence of the pressure on the rovibrational motion of CO in solid C₆₀, as deduced from IR absorption spectroscopy. CO intercalated C₆₀ samples [4] are loaded in the sample chamber of a compact high-pressure cell and their IR transmis-

sion spectrum is recorded using a Fourier transform infrared absorption spectrometer (Bruker IFS 66v) in combination with an IR microscope. The sample chamber is a small 0.5 mm diameter hole drilled in a brass gasket that is preindented down to approximately 30 μm thickness. No pressure transmitting medium is used or needed as C₆₀ may be seen to act as a perfect pressure transmitting medium itself [7] and as intercalation of C₆₀ with species other than CO needs to be avoided in this study [8]. The high-pressure cell is of the type as described by others [9] and consists of two identical 6.35 mm diameter sapphire balls on which facets of approximately 1.5 mm diameter are polished perpendicular to the *c* axis. It has been experimentally demonstrated that pressures above 100 kbar can be obtained with a similar cell [10]. Sapphire is fully transparent from the ultraviolet to about 5 μm in the IR, and is thus well suited for a spectroscopic study in the spectral region of the CO stretch vibration ($\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$). Unfortunately, the four allowed IR modes of C₆₀ escape observation, but numerous combination bands above 2000 cm⁻¹ can be used for relative pressure calibration and to monitor structural changes in the C₆₀ lattice with pressure. Absolute pressure calibration is performed using the ruby fluorescence method [11].

In Fig. 1(a) the room temperature IR absorbance of the CO intercalated C₆₀ sample is shown in the 2000–2250 cm⁻¹ region for zero pressure and for a pressure of 8.5 kbar. All sharp features in the zero pressure spectrum of the CO intercalated C₆₀ sample are due to combination bands of C₆₀ [12], and for comparison a room temperature, zero pressure, spectrum of pristine C₆₀ is shown in Fig. 1(b). At zero pressure, the additional spectral structure due to the presence of CO can be recognized in the spectrum as a broad envelope throughout the 2050–2200 cm⁻¹ region with a peak centered around 2127 cm⁻¹. Upon increasing the pressure, the C₆₀ combination modes shift to higher frequency and broaden slightly with a concomitant decrease in peak intensity. The CO resonance, on the other hand, gains dramatically in peak intensity and becomes the dominant and most

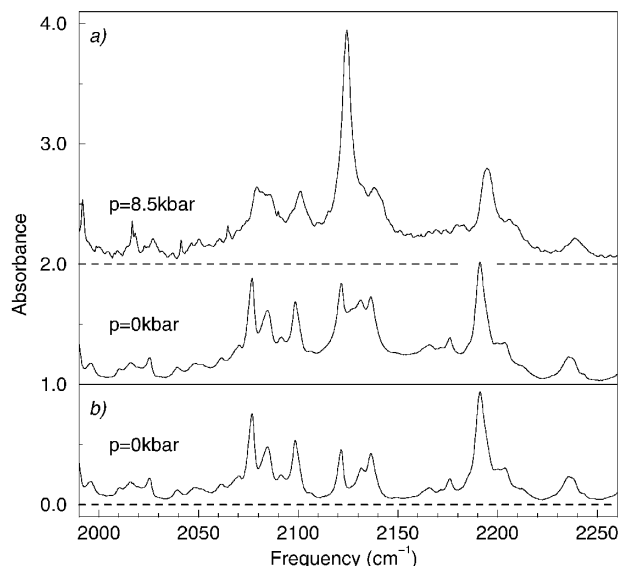


FIG. 1. Room temperature IR absorption spectra of (a) CO intercalated C_{60} at 0 kbar and at 8.5 kbar, and of (b) a thin film of pristine C_{60} under ambient conditions, measured at a spectral resolution of 0.5 cm^{-1} .

narrow feature in the spectrum for pressures above 10 kbar. The frequency shift of the most prominent C_{60} combination modes with pressure is tabulated in Table I.

In Fig. 2 the room temperature IR absorbance that is due to the presence of CO in the octahedral sites of solid C_{60} is shown in the $1950\text{--}2300 \text{ cm}^{-1}$ region for four different pressures. The spectra shown are the difference spectra of the IR absorbance spectra of a CO intercalated C_{60} sample and that of a reference pristine C_{60} sample, taken at the same pressure. Because of a slight mismatch in pressure and/or thickness between the CO intercalated C_{60} and the pristine C_{60} sample, the strongest combination bands (most notably around 2075 cm^{-1} and around 2190 cm^{-1}) are not completely corrected for using this procedure. It is evident from the spectra shown in Fig. 2 that the central peak becomes narrower and gains in intensity, at the cost of the intensity in the wings, when the pressure is increased. The wings do not only decrease in intensity relative to the peak but they also flatten and actually extend substantially further with increasing pressure. The integrated intensity of the spectral structure due to CO stays the same (to within 5%) over the complete 0–32 kbar range. The central position of the CO peak is seen to shift to lower frequencies at a rate of $-0.16(1) \text{ cm}^{-1}/\text{kbar}$. Up to approximately 40 kbar, the observed changes in the spectra as shown in Fig. 2 are fully reversible.

Prior to presenting the theoretical model, some details on the orientational order in (CO intercalated) C_{60} need to be discussed. It is well documented that solid C_{60} transforms from the ambient fcc rotator phase, to an orientationally ordered simple cubic (sc) structure around 260 K [3]. Below the first order sc \leftarrow fcc phase transition, apart from

jump rotation between symmetry equivalent orientations, dynamic reorientation between two symmetry inequivalent orientations remains. These two orientations correspond to an electron-rich double bond on a C_{60} molecule facing an electron-poor region on each of its neighbors, either a pentagonal face (p orientation) or a hexagonal face (h orientation). Under ambient pressure the p orientation is energetically preferred, and gains in occupation relative to the h orientation when the temperature is decreased [13]. When pressure is applied to a C_{60} sample, the transition temperature of the first order phase transition increases, and the orientationally ordered sc phase exists at room temperature for pressures above 3–4 kbar [14,15]. As the lower-energy p orientation has a substantially larger volume than the h orientation, pressure favors the h orientation, and there is evidence that a room temperature C_{60} sample at pressures somewhere above 10 kbar predominantly consists of h -oriented molecules [16,17]. From a recent x-ray analysis under ambient pressure, it is concluded that the presence of CO in the octahedral sites does not change the low temperature crystal structure, apart from a slight dilatation of the lattice. Interestingly enough, CO apparently further stabilizes the lowest-energy p orientation [18].

In order to understand the observed pressure effects in the infrared spectrum, quantum mechanical model calculations are made. The interaction of a molecule like CO with the surrounding C_{60} molecules in the solid is due to van der Waals interactions and steric hindrance; it can be represented by an atom-atom potential. We assume that rigid C_{60} molecules with a fixed orientation are positioned on an fcc lattice. The potential felt by CO is due to the combined interaction with the surrounding C_{60} nearest and next-nearest neighbors, and is rather sensitive to the orientation of the C_{60} molecules. In this potential we calculate the center of mass, i.e., translational, motions of the CO molecule, as well as its (hindered) rotations, implying a total of 5 degrees of freedom. Because of the rather complex shape of the van der Waals potential surface, there is strong translation-rotation coupling and quantum mechanical tunneling between equivalent minima, so that a full five-dimensional quantum mechanical treatment [4,19] has to be given. First we calculate the bound states for a rigid CO molecule inside this potential, and next, with the aid of a dipole function which represents the CO

TABLE I. Frequency shift of the dominant C_{60} combination modes with pressure in a pristine C_{60} sample. The values in parentheses are the uncertainties in the last digits.

| $\nu_0 \text{ (cm}^{-1}\text{)}$ | $\frac{d\nu}{dp} \text{ (cm}^{-1}\text{/kbar)}$ | $\nu_0 \text{ (cm}^{-1}\text{)}$ | $\frac{d\nu}{dp} \text{ (cm}^{-1}\text{/kbar)}$ |
|----------------------------------|---|----------------------------------|---|
| 2076.9(2) | 0.44(2) | 2348.8(2) | 0.31(2) |
| 2136.5(2) | 0.35(2) | 2677.9(2) | 0.88(5) |
| 2191.1(2) | 0.45(2) | 2737.1(2) | 0.89(4) |
| 2328.0(2) | 0.35(2) | 2911.2(2) | 0.82(4) |

stretch transition dipole moment, we synthesize the room temperature IR absorption spectrum. This procedure is repeated for different values of the lattice constant corresponding to the different pressures used in the experiments.

An aspect that is not considered in the theory is that the C_{60} lattice is not rigid. This would have to be taken into account by including also the lattice dynamics of solid C_{60} or, in other words, by including the coupling with the phonons and librions of the lattice that give rise to periodic deformations of the cavities. Above the orientational ordering phase transition [3], the motions of C_{60} in the lattice will mainly give rise to spectral line broadening. Since below the orientational ordering phase transition the motions of the C_{60} molecules are severely restricted [20], substantially less line broadening is expected in this case. This is evidenced in Fig. 2 as an abrupt narrowing of the central peak in passing the phase transition between 3.2 and 8.5 kbar. As details on the broadening mechanism are not known at this stage, the calculated stick spectra for lattice constants corresponding to the pressures used in Fig. 2 are convoluted with a Gaussian line shape with a full width at half maximum of 2.5 cm^{-1} . The calculated spectra are shown in Fig. 3. The central peak in these spectra corresponds to the excitation of the pure CO stretch vibration, and the wings are due

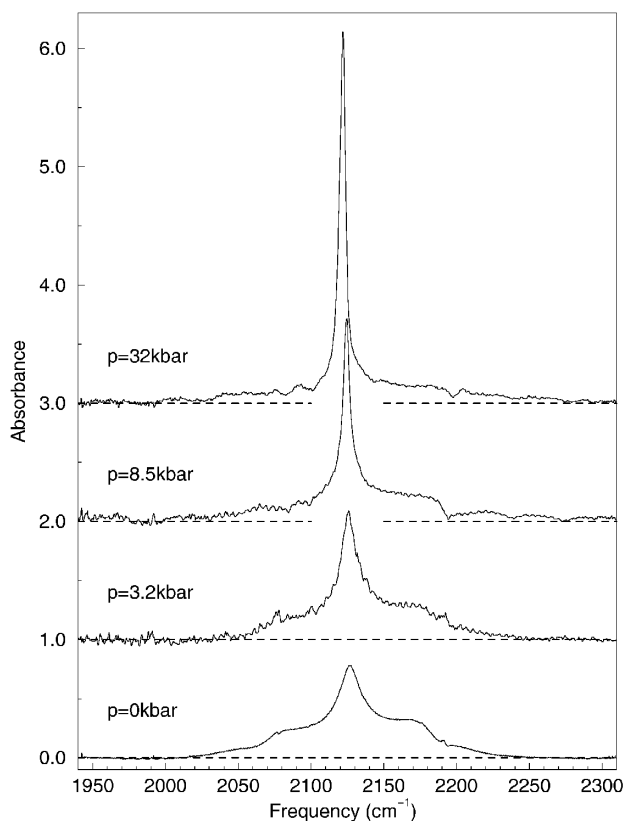


FIG. 2. Room temperature IR absorbance due to the presence of CO in the octahedral sites of solid C_{60} as a function of pressure, measured at a spectral resolution of 0.5 cm^{-1} .

to sideband transitions between levels associated with the translational vibrations and librations of CO in the cavity, starting from all thermally populated lower levels. Both the experimentally observed increase of the central peak and the broadening and flattening of the wings with increasing pressure are well reproduced in Fig. 3.

If we assume the C_{60} molecules to be perfect spheres, then there are eight equivalent "pockets" in each octahedral cavity in which the CO molecule can be located, with equilibrium orientations of the CO axis along the body diagonals of the conventional cubic cell. When the C_{60} molecules are orientationally ordered, the symmetry of the site is reduced to S_6 . It is found that the six symmetry equivalent minima off the C_3 axis are the global minima, while the two symmetry equivalent minima on the C_3 axis represent local minima [4]. In Fig. 4(a) the depth of the global minima is shown as a function of lattice constant, and is seen to be rather constant over the range probed in the experiments. At the same time the barrier for jumping between equivalent global minima, which is shown in Fig. 4(b), is seen to significantly change, however. This change of the barrier with lattice constant will severely restrict the motion of CO with increasing pressure, which

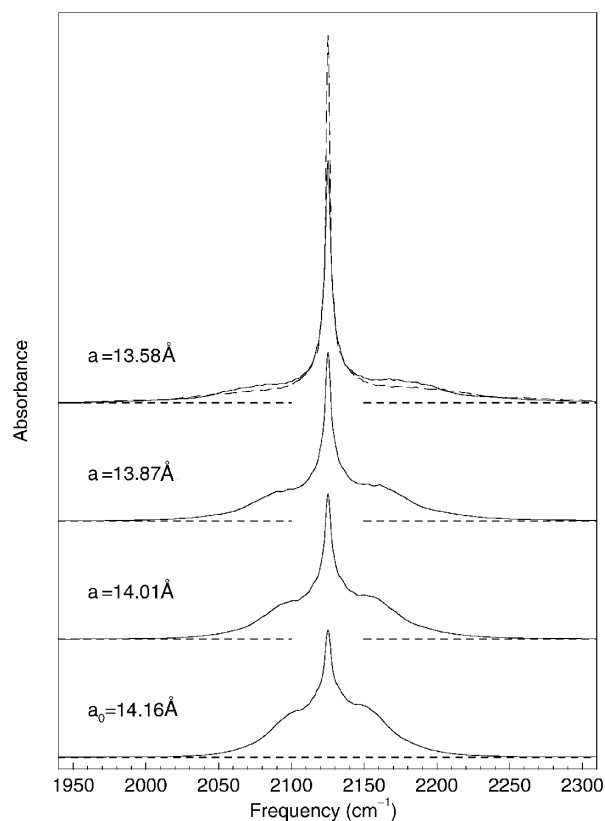


FIG. 3. Calculated IR absorption spectra of CO in the octahedral sites of solid C_{60} for four different values of the lattice constant, corresponding to the four experimental situations shown in Fig. 2. The calculations have been performed with all C_{60} molecules in the p orientation (solid lines) and with all C_{60} molecules in the h orientation (dashed line).

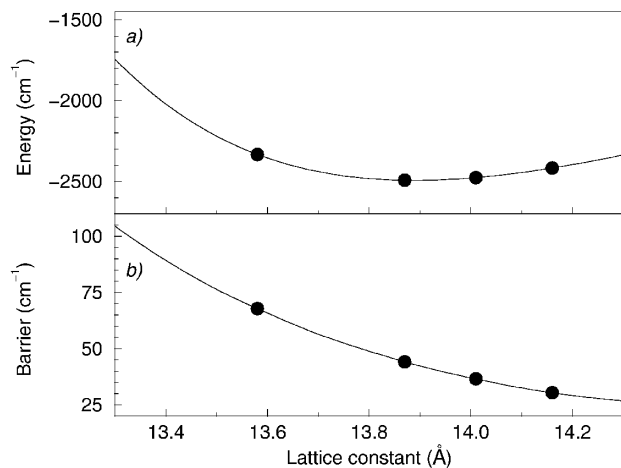


FIG. 4. (a) Calculated minimum potential energy of CO in the octahedral site of solid C_{60} and (b) calculated lowest barrier between two symmetry equivalent global minima as a function of lattice constant. The maximum diameter of the sphere that can be enclosed in the octahedral site is equal to the lattice constant minus the van der Waals diameter of a C_{60} molecule (≈ 10.0 Å). The calculations have been performed with all C_{60} molecules in the p orientation. The dots indicate the lattice constants used in the calculations shown in Fig. 3 and correspond to the pressures used in the experiments shown in Fig. 2, assuming the same compressibility for CO intercalated and pristine C_{60} [7].

explains the increase of the central peak in the IR absorption spectrum. The broadening of the wings in Figs. 2 and 3 is caused by an increase in the frequencies of the translational vibrations and librations of CO with the reduction of the cavity size.

The calculation with the smallest lattice constant, to be compared to the spectrum at 32 kbar, is performed both for all C_{60} molecules in the p orientation (solid line, Fig. 3) and for all C_{60} molecules in the h orientation (dashed line, Fig. 3). Although not conclusive, the experimental data are in best agreement with the h orientation, which is the preferred orientation for pristine C_{60} at high pressure as well. The agreement between theory and experiment shows that CO intercalated C_{60} truly behaves as a “molecule in a box” and that a large part of the transition from translationally and rotationally free molecules in a box to rigidly oriented molecules can be studied experimentally and described accurately by theory.

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