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# Spectroscopic observations of the displacement dynamics of physically adsorbed molecules—CO on C<sub>60</sub>

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## ABSTRACT

In this paper, we observed physically adsorbed CO molecules on C<sub>60</sub> surface being displaced by impinging noble gas atoms (He, Ne, Ar, Kr), either through a dynamic displacement process or an exothermic replacement process, depending on their adsorption energies. This displacement mechanism could shift from one to the other depending on the surface coverage and temperature. Furthermore, rotational energy of the impinging molecules may also contribute to the dynamic displacement process by supplying additional energy.

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## 1. Introduction

The physical adsorption of molecules on surfaces under equilibrium conditions provides the basis for a wide-range of sorption technologies used to purify gas streams as well as for the adsorption of contaminants from liquids containing dissolved substances. High area carbon surfaces are often used for such technical adsorption processes [1]. Physical adsorption also provides the basis for the determination of the surface area of powdered materials through isotherm fits [2,3], including the widely used BET method [4]. Under adsorption conditions, the adsorbed layer exists in dynamic equilibrium with the gas or liquid phase. In this work, we probe the effect of competing physisorbed gases on the equilibrium layer and report observations which give insight into the dynamics of displacement of one physisorbed molecule by another. Such displacement processes are important in technological sorption processes since displacement of a one sorbate by another sorbate molecule could defeat the purpose of the adsorption process.

The dynamical displacement process may be similar to the mechanism of collision-induced desorption and dissociation of chemisorbed adsorbates on metal substrates, which has been studied in the past. Yates and Goodman [5] found that the presence of CO gas enhanced the desorption rate for CO on Ni(100), and they believed it is a result of CO–CO repulsive lateral interaction lowering the CO chemisorption energy. The involvement of physisorbed CO species in forcing the replacement of chemisorbed CO was excluded. The dynamical process as well as the CO adsorption energy on Ni(100) have also been studied by others, confirming the repulsive interaction model [6]. Similarly, Takaoka et al. observed collision-induced migration of CO on Pt(997) surface [7]. However, these studies are related to CO chemisorption whereas the present work concerns the physisorption of CO.

The C<sub>60</sub> molecule provides a convenient high area carbon surface for physical adsorption studies. Its geometrical surface area of 1287 m<sup>2</sup>·g<sup>-1</sup> consists of two parts—that on the geometrical outer surface and that buried in the crystal structure of the solid C<sub>60</sub>. We have used CO as the physisorbed molecule of interest since it is active in the infrared spectral region permitting its observation at the fractional monolayer level. Our spectroscopic measurements of the infrared lineshape of physisorbed CO indicates that under the low pressure conditions of this experiment, only surface-bound CO is being adsorbed. Much higher pressures of CO are needed to occupy the interior sites which exist between C<sub>60</sub> molecules in solid crystalline C<sub>60</sub> [8]. The physisorption of CO on the surface of solid C<sub>60</sub> at cryogenic temperatures was first observed by Folman and colleagues [9,10] using transmission IR spectroscopy to study adsorption on an evaporated C<sub>60</sub> film. A strong ν(CO) absorption band was observed at 2128 cm<sup>-1</sup> at temperatures near 77 K.

The physical adsorption of other gases on C<sub>60</sub> surfaces has been studied. For example, Trasca et al. [11] studied noble gases adsorption on a C<sub>60</sub> monolayer theoretically and experimentally, and phase transitions on the surface have been found to occur involving different site locations on the hexagonally close-packed C<sub>60</sub> surface. The energy changes associated with these transitions are small compared to the adsorption energy.

The general principles reported here are likely to apply also to technological carbon surfaces. The use of a highly uniform C<sub>60</sub> substrate for these studies permits one to see details of behavior which would be difficult to measure and interpret on more heterogeneous carbon surfaces.

## 2. Methods

The experiments were carried out in an high vacuum stainless steel cell (1.9 L), with a base pressure of 1 × 10<sup>-8</sup> Torr. As shown in Fig. 1, the C<sub>60</sub> sample was prepared using an evaporation method. In

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order to support the  $C_{60}$  sample, pre-dried KBr powder was pressed into a tungsten grid to make an IR transparent support, and then the grid was mounted on two Ni clamps [12]. This grid can be cooled by  $N_2(l)$  held in a rotatable support Dewar. A type K thermocouple was welded onto the grid. The grid could be electrically heated and the temperature can be controlled to  $\pm 0.1$  K using a LabView program which monitors the output of the thermocouple. The  $C_{60}$  powder was obtained from MER Corporation. The powder was transferred into a Macor crucible that faces the grid containing the KBr support, as shown in Fig. 1. The crucible was electrically heated with a coiled tungsten wire and the  $C_{60}$  temperature was measured by an internal type K thermocouple.

Before evaporation, both the KBr support and  $C_{60}$  powder were heated to 400 K and degassed for 1 h. Then the KBr support was cooled to 82 K using  $N_2(l)$  and rotated to face the crucible while the  $C_{60}$  inside the crucible was heated to 673 K in high vacuum. At 673 K,  $C_{60}$  sublimates from the crucible and is deposited onto the cold KBr support surface. IR measurement of the sample was used to monitor the growth of the  $C_{60}$  layer. The development of four fundamental modes of  $C_{60}$  at 1431, 1182, 576, and 526  $cm^{-1}$  is observed, as well as some small combination modes [13,14]. The thickness of  $C_{60}$  is estimated to be  $(4.5 \pm 1) \times 10^3$  monolayers of  $C_{60}$  molecules from its integrated IR absorbance [15]. The thickness of the  $C_{60}$  layer could also be measured using the period of the interference fringes in the  $C_{60}$  spectra over the frequency range of 2400–1000  $cm^{-1}$ , which gives an estimate of the  $C_{60}$  thickness of  $5 \times 10^3$  monolayers [8,14].

The  $C_{60}$  sample was annealed in vacuum at room temperature overnight after deposition. It was then cooled to the desired temperature during each experiment. CO and other noble gases were introduced into the cell through a precision variable leak valve. The pressure of the cell was recorded in three ways: a cold cathode which measures pressure below  $1 \times 10^{-4}$  Torr, a sensitive Baratron gauge which measures pressure between  $1 \times 10^{-4}$ , and 0.02 Torr, with a resolution of  $10^{-6}$  Torr; then a less-sensitive Baratron which measures pressure above 0.02 Torr, with a resolution of 0.001 Torr. Transmission IR spectra of the sample were measured by a Bruker Tensor 27 FTIR spectrometer with a  $N_2(l)$  cooled MCT detector. All spectra were measured at 4  $cm^{-1}$  resolution by averaging 128 scans. The entire spectrometer optical path was purged with dry,  $CO_2$  free air.

### 3. Results and discussion

#### 3.1. Adsorption of CO on $C_{60}$

Fig. 2 shows the progress of the physical adsorption of CO on  $C_{60}$  versus the CO background pressure. A single band at 2129  $cm^{-1}$  develops at constant wavenumber as the coverage increases at 110 K. The spectral FWHM, corrected for the 4  $cm^{-1}$  spectrometer resolution, is 6.9  $cm^{-1}$ ,

while Holleman and colleagues reported a  $\nu(CO) = 2127$   $cm^{-1}$  with a band FWHM = 2.5  $cm^{-1}$  for intercalated CO on  $C_{60}$  at 77 K when working at a spectrometer resolution = 0.2  $cm^{-1}$  [8]. Using the integrated absorbance of  $\nu(CO)$  and assuming that interactional effects between CO molecules do not seriously affect the infrared absorption coefficient, Fig. 2 shows that a Langmuir isotherm fits the data well. The reversible behavior of the adsorbed CO is strictly related to the CO pressure with no hysteresis effects, consistent with the expected behavior for a homogeneous surface. Using the known IR absorbance coefficient for CO(g) [16,17], we estimate that the saturation coverage of CO on  $C_{60}$  in our experiment involves a CO saturation coverage on the outer surface of the  $C_{60}$  of  $6 \times 10^{20}$  CO molecules  $\cdot m^{-2}$ . This coverage of CO indicates the high degree of porosity of the evaporated  $C_{60}$  film in the first  $\sim 100$   $C_{60}$  layers near the outer surface, which allows the occupancy of CO on the outer sites. The outer region available to CO adsorption is about  $10^{-2}$  of the  $C_{60}$  film thickness. The interior sites investigated by Holleman et al. [8] are not populated at the low CO pressures employed here.

Using the integrated infrared absorbance as a measure of equilibrium surface coverage, a set of partial isotherms were measured at temperatures in the range 82–130 K, as shown in Fig. 3a. By observing the coverage,  $\theta_{CO}$ , at 0.001 Torr CO equilibrium pressure, an isobaric enthalpy of adsorption was measured and was found to be  $-0.109 \pm 0.004$  eV, as shown in Fig. 3b. This is in good agreement with theoretical calculations of the enthalpy of adsorption of CO on  $C_{60}$ 's fcc (111) plane where an energy of adsorption of  $-0.13$  eV was calculated [10]. Jiang et al. also compared the CO and  $N_2$  physical adsorption energies and the adsorption sites on the  $C_{60}$  surface [18]. The linearity of the data in Fig. 3b is consistent with little CO–CO interaction over the range of coverage studied here.

#### 3.2. Displacement of physisorbed CO by He, Ne, and Ar

We observed the monotonic displacement of physisorbed CO by He, Ne, and Ar, when these noble gas molecules were introduced into the chamber. These data were obtained at 110 K under equilibrium conditions with a constant  $P_{CO} = 0.01$  Torr, as shown in Fig. 4. The displacement process is plotted against the calculated flux,  $F_x = \frac{P_x}{(2\pi m_x k_B T)^{1/2}}$ , of each added gas, assuming a gas temperature equal to that of the walls of the infrared cell, 300 K. As the displacing gas flux increases, additional CO desorption occurs, disturbing the equilibrium and producing a decrease in the equilibrium value of  $\theta_{CO}$ . One notes that as the mass and the polarizability of the displacing gas atom increases (polarizability of He = 0.208  $\text{\AA}^3$ ; Ne = 0.381  $\text{\AA}^3$ ; Ar = 1.664  $\text{\AA}^3$  [19]) the degree of displacement of equilibrium adsorbed CO at a given  $F_x$  decreases. This means that two effects may operate together in governing the displacement efficiency: (1). The van der Waals forces involved in the

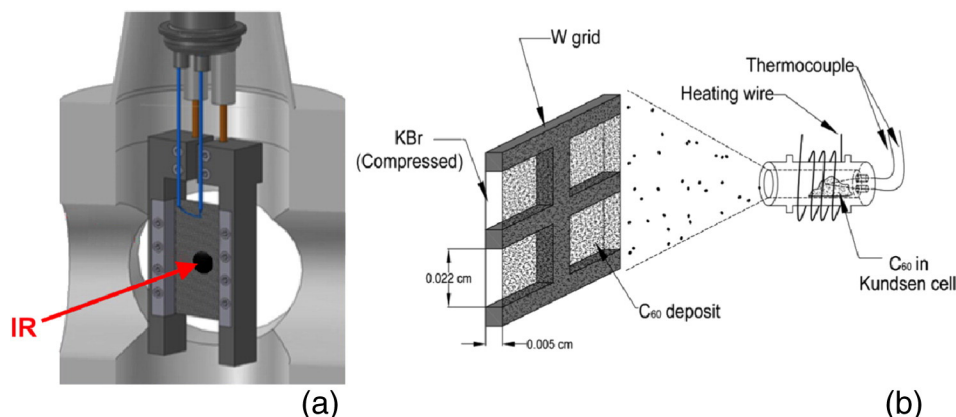


Fig. 1. (a) The configuration of KBr support pressed on a tungsten grid in the IR vacuum cell. (b) The evaporation process of  $C_{60}$  onto the KBr support.

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