Laser desorption of NO from a thick C_{60} film

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Abstract

The desorption of NO molecules from a thick C_{60} film is reported. A thermal desorption spectrum indicates two adsorption sites with binding energies of $E_b = 0.30$ eV and 0.55 eV. For laser desorption the fullerene surface is exposed to NO and excited by 7 ns UV laser pulses. Desorbing NO molecules are recorded state selectively as well as time resolved. The time-of-flight measurement indicates three different desorption pathways. A fast channel shows rovibronic temperatures of $T_{rot}(v'' = 0) = 370$ K, $T_{rot}(v'' = 1) = 390$ K and $T_{vib} = 610$ K as well as strong rotational–translational coupling. The desorption yield for the fast channel increases linearly with pulse energy with a desorption cross section of $\sigma = (5.1 \pm 0.9) \times 10^{-17}$ cm^2. Dominating the signal for small J'' values is a slow channel with low rotational and translational temperatures of about 110 K. We assign this peak to a laser-induced thermal desorption. For large pump–probe delays the data deviate from the Maxwellian flux distribution and a third channel appears with extremely late arrival times.
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1. Introduction

The understanding of dynamical processes on surfaces plays an important role in controlling surface reactions. In this context the fullerenes are of great interest because of their size, symmetry, and electronic properties. A pristine C_{60} surface builds a face-centered cubic (fcc) structure in which the cages are able to rotate freely at room temperature. This rotation freezes below a glass transition temperature of $T_{01} \simeq 260$ K and the structure is changed to simple cubic (sc) in which only one rotational degree of freedom remains. The conformation in which the electron-rich double bond of two pentagons faces a pentagon is the energetically lowest, the conformation in which this bond faces a hexagon is, however, only a few meV higher. This locking-in transition where ordering begins occurs at a temperature of $T_{02} \simeq 90...120$ K [1,2].

The interaction of C_{60} surfaces with atoms or molecules has only rarely been investigated under UHV conditions.

Fastow et al. used IR spectroscopy to firstly examine NO and CO on C_{60} [3] at a surface temperature of $T_s = 78$ K, and concluded that NO adsorbs as a dimer $(NO)_2$ and revealed the possibility of diffusion into the octahedral and tetrahedral sites. Later they characterized the adsorption on different sites, too [4]. The adsorption sites of CO in C_{60} are investigated both by X-ray diffraction and NMR in C_{60} powder after intercalation of CO with a pressure of $p \approx 200$ bar by Meijer and coworkers [2,5]. They observed an increase of the lattice constant by 3 pm which slightly increases between 100 and 200 K. When intercalated with CO the glass transition around 90 K ceases and CO exclusively occupies one of the six positions in the octahedral sites. The high pressure measurements also revealed a charge transfer from the molecule, e.g., CO, NO, or O_2, to the fullerenes [2,6,7], associated with an increase in binding energy. Gu et al. [7] estimated a charge transfer of $q = 0.065$ electrons. Recent theoretical studies support this observation for CO and NO [8,9]. NO stabilizes the fullerene matrix up to temperatures of 1600 K with a charge transfer of 0.06 electrons. From these measurements the diffusion of molecules through C_{60} is known to be slow (O_2 in C_{60}: 2000 Å/30 min $\approx$ 1 ML in 10 s)

[10,11] and the concentration decreases with the distance from the surface. Unfortunately, the interaction of NO with C_{60} is not as well studied as that of CO and O_2. NO has a larger dipole moment than CO and thus a larger binding energy to C_{60} is expected.

The optical absorption spectrum of C_{60} vacuum deposited on quartz has three maxima at 3.6, 4.6 and 5.5 eV. They are associated with electronic excitations to various short-lived LUMO bands [12]. In addition long living excited triplet states are present in C_{60}. These states are known to be electronically active [13]. But their interaction with adsorbates has not been studied yet. In this paper we report on rotational populations after laser desorption of NO by scanning the $\gamma(0 \leftarrow 0)$ and $\gamma(0 \leftarrow 1)$ bands of NO. For a given spectral resonance the delay between pump and probe laser can be varied to examine the velocities of the desorbed molecules. Further, binding energies of NO on C_{60} are analyzed by thermal desorption spectroscopy (TDS).

2. Experimental

The experimental set-up consists of a UHV chamber with a base pressure of 3×10^{-10} mbar during operation and a laser system which is operated at 10 Hz. The UHV chamber is divided into a preparation and a desorption chamber. The preparation chamber includes a C_{60} evaporator, a sputter gun, an electron spectrometer and the usual surface examination tools (UPS, LEED, AES, XPS). The sample consists of either a polished poly-Cu or a Cu(1 1 1) single crystal substrate and an annealed and slowly grown C_{60} film. The sample can be cooled by liquid nitrogen to a temperature of 110 K which is sufficiently low to bind NO on C_{60} (see Section 3). An electron beam heated evaporator doses C_{60} in a controlled beam onto the surface at room temperature. The surface is annealed at 400 K for 20 min thereby forming a fcc structure. To avoid polymerization the sample is cooled by liquid nitrogen afterwards. In the desorption chamber a pulsed supersonic valve doses nitric oxide through two skimmers and two differential pumping stages onto the sample mounted on a cryostat. The re-dosing after laser desorption amounts to about 20% of the saturation coverage.

A pulsed Nd:YAG laser (Quanta Ray DCR-11, 355 nm, 7 ns) desorbs NO molecules from the surface. The first absorption band belongs to the HOMO $\leftrightarrow$ LUMO+1 excitation [14] and is in resonance with the excitation wavelength. The beam is focussed through a 300 mm quartz lens at an angle of 85° to the surface normal giving an ellipsoidal spot of 0.11 cm^2 on the sample at a fluence of 3 mJ/cm^2. The intensity is well below the critical value of 20 mW/mm^2 for which uncooled C_{60} polymerizes [15]. The irradiation raises the temperature of the C_{60} film by about 20 K. Due to a tilted sample the incident radiation consists of 26% ŝ- and 74% p̂-polarization.

The detection of NO is performed by a frequency doubled dye laser (PDL-3, Spectra Physics, $\Delta \tilde{v} \approx 0.07$ cm^{-1})

pumped by the third harmonic of a Nd:YAG laser (Quanta Ray GCR-230). After an adjustable flight distance of 17–25 mm NO molecules are resonantly excited in the γ-bands around 226 nm ($A^2\Sigma \leftarrow X^2\Pi$) and ionized by absorption of a second photon of this radiation (1 + 1 REMPI). The ions are separated by a reflectron time-of-flight mass spectrometer and detected by micro channel plates.

The TDS measurements are accomplished in a different UHV chamber. It is equipped with a C_{60} covered Cu(1 1 1) crystal which is cooled by liquid nitrogen to a temperature of $T_s = 92$ K. Electronically controlled electron impact heats the sample linearly with adjustable rates. The temperature ramp is controlled by a thermocouple welded to the side of the sample.

3. Results and discussion

3.1. Thermal desorption

Fig. 1 shows a TDS spectrum of NO from a thick C_{60} film obtained with a heating rate of $\beta = 5$ K/s. Beginning at 92 K a maximum desorption flux at a temperature of 120 K followed by a long tail towards higher temperatures is observed. In this tail a second broad peak at 210 K can be recognized. The peak at 120 K corresponds to a pre-exponential of 6.8×10^{12} s^{-1} and a binding energy of $E_{b1} = 23$ kJ/mol. This peak may be due to NO on atop sites. The broad peak yields a pre-exponential of 1.2×10^{13} s^{-1} and a binding energy of $E_{b2} = 53$ kJ/mol. It might be caused by NO intercalated in the C_{60} bulk. When diffusing out slowly it also produces a long tail towards high temperatures. Below 100 K no desorption of NO is identified.

Folman and co-workers examined NO on graphite [16] as well as on C_{60} [3] using IR spectroscopy at liquid nitrogen temperature. They concluded from the successive appearance of two double peaks that NO is adsorbed as a
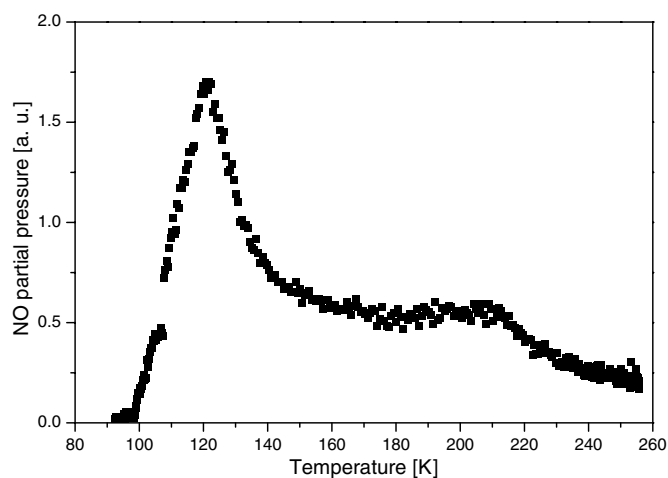

Fig. 1. Thermal desorption spectrum of NO from C_{60}/Cu(1 1 1) showing two adsorption sites at a heating rate of $\beta = 5$ K/s with desorption temperatures of 120 K and 210 K.