STM induced rotacion of acetylene molecules adsorbed on Pd(111).

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Abstract

Images of acetylene molecules have been obtained by Scanning Tunneling Microscopy. The molecule can adsorb with three different and energetically equivalent orientations. The imaged molecules do not diffuse at 44K, however they hop between the three different orientations. This rotation rate is believed to be activated by the electronic current flowing at the interface. The rotation rate is analyzed as a function of the scanning current. The experimental curve is fitted to a theoretical expression, and the orders of magnitude of the vibrational frequency of the rotational mode and the inelastic current fraction are determined.

Introduction

Acetylene molecule is known to adsorb in a three fold position on the Pd (111) surface (ref.1). The C-C axis is parallel to the surface, and its center lays on the center of the triangle formed by the three substrate neighbouring atoms.Thus, the stable configuration has three possible equivalent orientations, rotated 120° with respect to each other. An STM image of the adsorbed molecule (ref. 2) displays a highly anisotropic shape, due to interaction of the molecular orbitals with the asymmetrically arranged substrate neighbours. This fact allows an easy identification of the molecule's orientation on the surface.

Acetylene manipulation via STM is of great importance, as it may help in studying at a molecular scale the reactions leading to the formation of benzene. A review of benzene tricyclization (including acetylene adsorption) has been done in ref. 1. Theoretical studies of the electronical structure, geometrical configuration and energetic configuration of the molecule have been extensively performed (refs.3-5).

Description of the experiment

The Pd (111) sample with adsorbed acetylene molecules was scanned at constant current. The temperature was 44K.The total corrugation of the molecules is about 0.2 when the gap is 100 MΩ, and increases about 50% when it is reduced to 10 MΩ. Due to the image asymmetry, the orientation of the molecule can be detected. When scanning, molecules jump from one orientation to another, remaining on the same adsorption site. This process manifests itself as a discontinuity in the image. Thus, it is possible to analyze the number of hops that take place per second, and study their dependence as a function of the current. We have plotted the logarithm of the rotation rate for a current varying in a range of 200 nA (fig. 1).

Though at 44K no diffusion between different sites is observed, raising the temperature leads eventually to intersite diffusion. Assuming a preexponential factor of 10^{13} (ref. 6) the estimated activation barrier for diffusion is about 180 meV .

Discussion.

In principle, one can think of several different mechanisms responsible for increasing the rotation rate of the molecules when they are scanned. Considering the rotation process as a jump of the molecule between two potential wells, one would first try to argue that electric field effects alone would be able to reduce the potential barrier between minima, thus enhancing the rotation probability. Such a mechanism is well known in studies of field induced surface migration (ref. 6), and its application to STM experiments has been reviewed in ref. 7. In order to check whether such an effect plays a role or not in our case, we have estimated, within an extended Hueckel calculation, the barrier reduction due to a field of 0.5 V/Å, resulting in a reduction of about 0.01 eV in the barrier height. The field estimated in the interface is of the order of 0.01-0.1 V/Å, what implies a barrier reduction of 1% with respect to the total barrier height (0.1 eV). Thus, the field effect is not believed to play any role in the enhancement of rotation probability. In what follows, we shall therefore consider that rotation is primarily induced by vibrational excitation due to collisions with electrons, in the way of ref. 8.

Following the analysis made by Walkup et al. (ref. 8) for the transition rate between two wells when an electric current is flowing, one can describe the energy distribution of vibrational states of the molecule as a Boltzman distribution, with an effective vibrational temperature that depends on the inelastic electric current fraction, the damping rates, and the frequency of the mode. One can estimate the rotation probability, P, as (ref. 8)

$$\log P=\log V+\frac{\Delta E}{\hbar\omega}\log\left(\frac{I\cdot f_{inel}+\gamma e^{-\hbar\omega/kT_s}}{I\cdot f_{inel}+\gamma}\right) \quad (1)$$

where T_s is the temperature of the sample, γ is the inverse of the vibrational mode's decay time, Υ is a prefactor in principle different than the usual vibrational frequency, and ω is the mode's vibrational frequency. Typical mode's decay times on metals are of the order of 10^{-11} s. The current is of the order of 10^{-12} s. The prefactor in eq. (1) is not the usual 10^{13}, but is given by (ref. 8)

$$\gamma\frac{\Delta E}{\hbar\omega}f_l \quad (2)$$

where ft is the probability that the state deexcites in the neighbouring well. In ref. 8 it is considered 0.5, as they assume deexcitation from a state whose energy is above the energy barrier. Within such assumption, our prefactor would be of the order of 10^{11}. We have fitted the experimental points to expression (1), taking the mode's vibrational frequency and the inelastic tunneling fraction as fitting parameters.The total height of the barrier for rotation has been taken as 113 meV, calculated in ref. 2, using the Vienna ab initio simulation program (ref. 9). γ was set as 10^{11}. The resulting fitting parameters are an energy of 0.041 eV for the rotational mode, and an inelastic fraction of 10^{-5}.

The first experimental point was not used for the fitting. The reason is that when the current is smaller the mechanism for rotation becomes a thermally activated one. Therefore, the prefactor will shift towards 10^{13}. As such an effect is not included in the theoretical expression, we prefer to skip the first point, for it falls apart from the trend followed by the other ones.

The inelastic fraction is one order of magnitude smaller than that obtained in ref.8 for the case of Xe transfer. Nonetheless, it is natural to expect a smaller inelastic fraction in this case, as the cross section to excite the rotational mode may be very small, and it is possible that the excitation takes place indirectly, via energy transfer from other mode previously excited. In general, the dipole mechanism is not able to excite the rotational

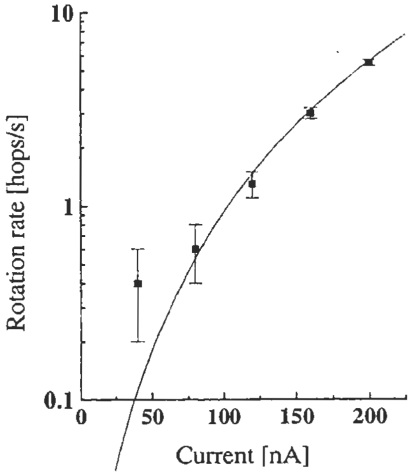

Fig.1 Experimental points corresponding to the measured rotation rate as a function of the current. The gap was kept fixed at 100 MΩ. Electrons flow from the tip to the sample. Temperature is 44 K. The solid curve represents the theoretical fitting of experimental points. The first of the points was not used in the fitting (see explanation in text).

mode (for it oscillates in the direction parallel to the surface) being only able to excite a vibration perpendicular to the surface. The fitting curve together with the experimental results is given in fig. 1.

Summary

We have been able to induce the rotation of adsorbed acetylene molecules when scanning them with STM at 44K. We have checked that the rotation rate enhancement is not related to electric field effects, but is due to excitation of molecular vibrational modes by the electric current that flows through the molecule. An effective "vibrational" temperature related to the electric current can be defined, giving rise to a Boltzman distribution of the molecule's vibrational states. Following the mechanism proposed in ref. 8, we can fit the rotation rate to a theoretical expression. The values obtained for the vibrational frequency and the inelastic tunneling fraction are 0.041 eV and 10^{-5} respectively.

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