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# Principles of operating molecular nanomachines by electronic excitation

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## Abstract

Powering and controlling the operation of a single molecule adsorbed on a surface can be achieved by using the tip of a scanning tunnelling microscope (STM) as an atomic-size source of electrons. We review the various electronic excitation processes induced by the electrons from the STM tip which are able to activate the functions of a molecular nanomachine. In particular, we review recent results illustrating the electronic control of molecular dynamics at the level of a single molecule.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

A molecular nanomachine should consist of a single molecule or a single designed molecular architecture of a few molecules having one or several specific functions, for example, electronic, mechanical or chemical. The concept of molecular nanomachines appeared in the 1990s, with the ability to power and to control the operation of a single molecule adsorbed on a surface by using a scanning tunnelling microscope (STM) [1]. Although other techniques (planar nanojunctions, break junctions) have been developed to isolate a single molecule and to use it, for example, for molecular electronics [2], the STM appears as the most flexible tool to explore the full range of molecular functions. We also emphasize that controlling the position and the environment of the molecule with an atomic-scale precision is generally required to properly operate a molecular nanomachine. The emergence of molecular nanomachines has greatly benefited from the developments of molecular machines in solutions [3]. However, in this case, a huge number of molecules are simultaneously activated through thermal, photochemical or electrochemical excitation [3]. It is interesting to note that the concept of molecular nanomachines has simultaneously appeared in biochemistry, where it has proved possible to monitor the movement of a single biological motor such as the ATP synthase [4].

Building and operating a molecular nanomachine requires expertise in a number of different areas: (i) the design and the synthesis of the molecule for developing a given electronic, mechanical or chemical function, (ii) the choice of the surface and its reactivity,

(iii) the method of deposition of the molecule, and (iv) the method for activating and controlling the operation of a single molecule. All four points are equally important. However, in this paper, we will concentrate on the fourth one, i.e. on the principles of operating a molecular nanomachine.

Laser photon excitation would be an interesting method to control the operation of a single molecule due to its ability to precisely tune (i) the amount of deposited energy, (ii) the excited internal molecular degrees of freedom, and (iii) the duration of the excitation down to the femtosecond regime. Furthermore, the quantum control of molecular dynamics is also possible through laser excitation [5]. However, the limited spatial resolution of optical excitations (of the order of the wavelength) is compatible with a single molecule operation only by diluting the number of molecules adsorbed on a surface [6] or by working in the high resolution spectroscopic regime of molecules trapped in matrices at low temperature [7].

The most powerful method which has been used so far for controlling the operation of a single molecule is the STM. Indeed, an STM can be used in many different modes, i.e. imaging [1], electronic and vibrational spectroscopy [8, 9], probing the molecular dynamics [10], and manipulation [11]. Furthermore, an STM has an ultimate spatial resolution as low as 10 pm, which enables one to reach a (sub) molecular resolution in real space [12]. In this paper, we will discuss the methods for the manipulation of single molecules with an STM, and in particular, the methods for electronic excitation of single molecules.

## 2. Electronic excitation of individual atoms and molecules

Electronic excitation of atoms and molecules is well documented for collections of species in gas phase [13], in solution [14], in multilayers [15], or adsorbed on surfaces [16]. Studies have been performed by using laser [14], synchrotron radiation [17] and electron impact [16] excitation. A large background of knowledge is now available for the control and understanding of the electronic excitation processes of collections of molecules in various environments as well as the ensuing dynamical processes such as ionization, fragmentation, desorption, change of configuration, and chemical reactions.

Electronic excitation of individual atoms and molecules can be performed by using the tip of an STM. Indeed, as early as 1987 [18], it had been realized that an STM could not only image surfaces with atomic-scale precision, but moreover be used to manipulate individual atoms and molecules [11]. Several methods of manipulation have been tested over the past 15 years. These include direct contact (van der Waals or chemical interaction) between the STM tip and the atom or molecule [19, 20], electric field effects [21], vibrational excitation [22] and electronic excitation [23]. It is sometimes difficult to distinguish between vibrational and electronic excitation. Indeed, it is well known from DIET (desorption induced by electronic transition) processes [16] that the dynamics rarely occurs when the system is in the excited electronic state, but rather occurs after electronic relaxation when the system has acquired vibrational energy in its electronic ground state. Furthermore, vibrational excitation with an STM is considered to occur, most of the time, based on the tunnelling of electrons through molecular electronic resonances [24]. In such a case, the difference between electronic and vibrational excitation is not very apparent. However, in the case of electronic excitation, the acquired vibrational energy depends on the lifetime and the dynamics of the electronic excited state [16]. This will be manifest experimentally by the observation of a clear electronic resonance or electronic threshold [12] in the manipulation cross section variation as a function of the surface voltage. We emphasize here that electronic excitation is a suitable tool for controlling the dynamics of the molecule. In particular, electronic excitation should enable the molecule to be excited into far from equilibrium conformations, resulting in very rapid, efficient and more easily

controllable molecular dynamic processes. For example, electronic excitation of an electron from a bonding to an anti-bonding orbital will bring the system into a far from equilibrium dissociative configuration whose dynamics is expected to be rapid and efficient. Delocalization of the excitation energy by coupling with other degrees of freedom is also expected to be reduced due to the rapid dynamics, thus allowing an easier control of the manipulation.

### 2.1. Advantages and difficulties of electronic excitation with an STM

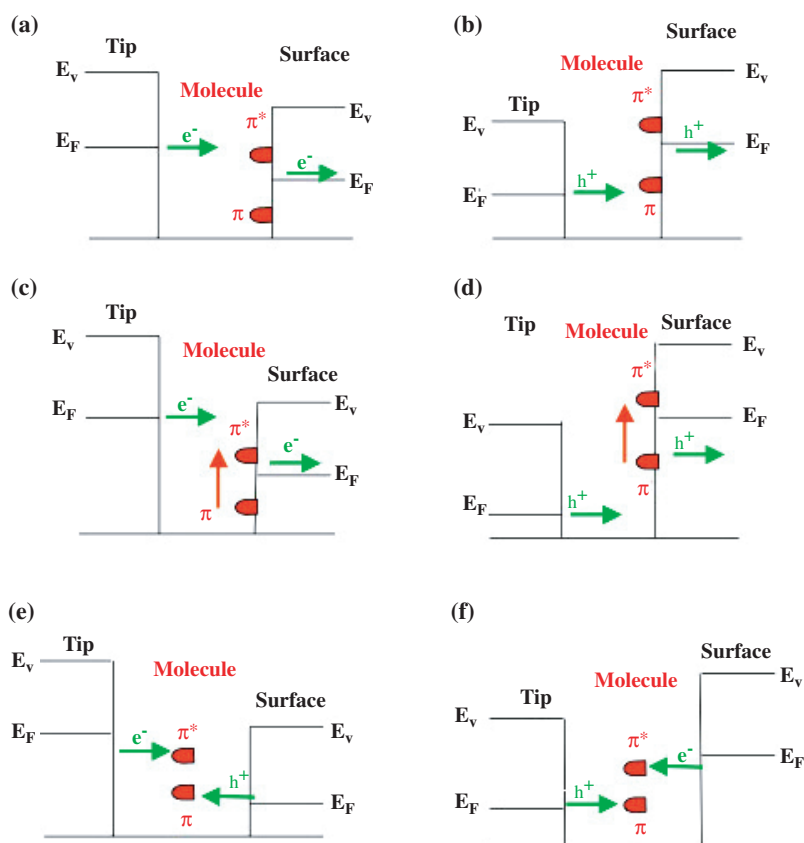
Using the STM tip to electronically excite a single atom or molecule offers a number of advantages and difficulties.

**2.1.1. Advantages.** The STM offers the possibility to combine, *in situ* with the same instrument, imaging, spectroscopy (both electronic and vibrational), excitation and probing the dynamics of a single atom or molecule. Furthermore, an STM has an ultimate spatial resolution as low as 10 pm at low temperature, which enables local electronic excitation to be performed, not only of a single atom or molecule but moreover inside a single molecule [12]. The actual spatial resolution of the electronic excitation is limited by the localization of the electronic states inside the molecule. The electronic processes under the STM tip offer a broad variety (see section 2.2) of different mechanisms. In particular, electrons from the tip can be injected into unoccupied electronic states of the atom or molecule. Such processes cannot be accessed through usual electron impact experiments on surfaces, except by inverse photoemission [25]. Another advantage is that an STM enables one to determine the precise position of each neighbour atom or defect. Indeed, it is now recognized that the electronic, mechanical (e.g. diffusion across the surface) or chemical properties of an individual atom or molecule can be strongly modified by the presence of a given atom in its neighbourhood [26]. For example, in a recent experiment on a bistable molecule (biphenyl adsorbed on Si(100)) [12], it has been found that the bistable switching yield was varying from one molecule to the other. Although the surface cleanliness and reconstruction was of very high quality [12], the atomic-scale environment could be different from one molecule to the other. In such a case where a low temperature STM is used and the molecular dynamics is reversible, all the quantitative studies can be performed with the same molecule. This ensures a complete reproducibility of the measurements which could not be guaranteed when working with many different molecules.

**2.1.2. Difficulties.** The precise identification of the electronic processes under the STM tip can be made difficult by the lack of knowledge of the electronic structure, at the atomic scale, of the occupied and unoccupied states of adsorbed atoms and molecules. STM spectroscopy can provide some information on the electronic structure. However, the presence of the STM tip close to the surface can modify the studied atomic and electronic structure either through direct contact between the STM tip and the surface or through the relatively strong electric field between the tip and the surface [27]. The electronic structure of the tip can play a significant role, modifying the observed electronic structure [28]. Furthermore, we note that both the electronic excitation and the probing of the molecular dynamics is achieved with the same tool, i.e. the STM tip [12]. This makes the realization of real pump–probe experiments difficult in a way that can be done more easily using two different lasers for exciting and probing the molecular dynamics. Finally, the tunnel current measurement is a very slow detection of molecular dynamics which is limited to timescales larger than about a millisecond.

### 2.2. Various types of electronic excitations with an STM

Using the STM tip as an atomic-size electron source can produce different kinds of electronic excitations, which are schematically shown in figure 1. In each case, the transport of electrons



**Figure 1.** Schematic diagrams of the electronic excitation processes of a molecule under the STM tip. (a) Electron attachment,  $V_S > 0$ ; (b) hole attachment,  $V_S < 0$ ; (c) electronic transition,  $V_S > 0$ ; (d) electronic transition,  $V_S < 0$ ; (e) electron-hole pair attachment,  $V_S > 0$ ; (f) electron-hole pair attachment,  $V_S < 0$ .

between the tip and the surface needs to dissipate some energy through inelastic electronic coupling in order to activate the electronic excitation of the adsorbed atom or molecule.

**2.2.1. Electron (hole) attachment.** Electrons from the STM tip can be attached temporarily onto unoccupied orbitals of an adsorbed atom or molecule, producing a negatively charged species (figure 1(a)) [24]. This requires a positive voltage on the surface,  $V_S > 0$ . Such a process has been considered to explain the desorption of hydrogen atoms from hydrogenated Si(100) [29, 30] and Ge(111) [31] surfaces through the attachment of electrons onto the  $\sigma^*$  (Si-H) and  $\sigma^*$  (Ge-H) anti-bonding orbitals respectively.

However, the resonant character of the process has not been clearly established, mainly because, when the electron energy is below the  $\sigma^*$  resonance energy (off resonance), multi-electron processes occur [29, 30]. Similar processes have been considered to explain the STM tip-induced desorption of individual CO molecules from a Cu(111) surface [32]. The attachment of electrons into highly excited unoccupied states of individual porphyrin molecules adsorbed on an ultrathin alumina film grown on a NiAl(110) surface has been assumed to induce light emission [33].

In contrast, holes can be attached to occupied orbitals (figure 1(b)), producing a positively charged species. This requires a negative voltage on the surface  $V_S < 0$ . With this method, hydrogen atoms have been desorbed from the hydrogenated Si(100) surface [34].

A comprehensive study illustrating both the electron and hole attachment processes has been performed on the desorption of chlorobenzene molecules from Si(111)- $7 \times 7$  [35]. Negative and positive ion resonances were assigned to the  $\pi$  orbitals of the benzene ring.

In fact, both elastic and inelastic tunnelling of electrons (holes) from the tip can occur through the unoccupied (occupied) orbitals of the adsorbed atom or molecule. The quantum efficiency of the inelastic process (number of inelastic events relative to the total number of tunnelling electrons) can vary within a very broad range, typically from  $10^{-10}$  to  $10^{-4}$ , depending on the system studied [23].

**2.2.2. Electronic transition.** Inelastic tunnelling of electrons (figure 1(c)) or holes (figure 1(d)) can also induce an electronic transition, i.e. the transition of an electron from an occupied orbital to an unoccupied orbital, in the adsorbed atom or molecule. This process should occur at a higher surface (tip) voltage compared to the electron (hole) attachment, such that the electrons are no longer in the tunnel regime but rather in the field emission regime.

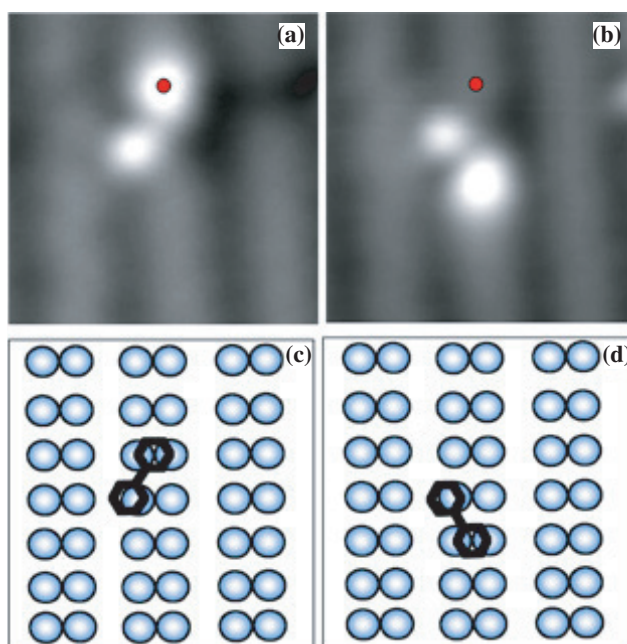
The best documented example is the  $\sigma \rightarrow \sigma^*$  electronic transition of the Si-H bond producing the desorption of individual hydrogen atoms from the hydrogenated Si(100):H surface [29]. This electronic transition occurs at a surface voltage of  $V_S \approx 8$  eV, which indicates that the electrons are emitted by the STM tip in the field emission regime. This electronic transition producing the desorption of hydrogen atoms has been also investigated by laser excitation [36, 37].

We emphasize that inelastic tunnelling of electrons or holes can also induce the emission of photons in the tunnel junction [38]. Such an emission of photons is in competition with electronic transitions.

**2.2.3. Electron-hole pair attachment.** Another type of electronic excitation of a molecule is the simultaneous attachment of an electron into an unoccupied  $\pi^*$  orbital and a hole into an occupied  $\pi$  orbital (figures 1(e) and (f)). Such an electronic scheme can only occur if the molecule interacts weakly with both the STM tip and the surface. In such a case, the orbital energies of the molecule can be shifted by the electric field between the tip and the surface, as shown in figures 1(e) and (f). This electronic process has been put forward to explain the STM tip-induced fluorescence of individual  $C_{60}$  molecules adsorbed on a NaCl ultrathin film grown on Au(111) [39].

### 3. Electronic control of molecular dynamics

We will review here the main examples of molecular dynamics which have been studied by electronic excitation with an STM. Most of these studies are concerned with irreversible dynamical processes [40, 41], in particular molecular dissociation [1, 42]. However, recently, a reversible dynamical process, namely the bistable movement of a single molecule, has been explored [12]. The concept of control has also greatly changed over time. Initially, control implied the ability to trigger the molecular dynamics by applying a pulsed voltage between the STM tip and the surface. The only control parameters were the surface voltage  $V_S$ , the tunnel current  $I_S$ , and the duration of the excitation. With the advent of more comprehensive studies, the concept of control has evolved to include having at least two different molecular dynamical channels and being able to activate each of them selectively. For that purpose, further control parameters, in particular the localization of the electronic excitation inside the molecule, have been recently experimented. There exist also several methods to monitor the dynamics of a



**Figure 2.** (a) and (b) 9 nm by 9 nm STM topographies ( $V_S = -2$  V,  $I = 0.2$  nA) of a biphenyl molecule on a Si(100) surface at 5 K showing the two stable positions of the bistable molecule. The dot indicates the STM tip position during the electronic excitation. (c) and (d) show schematically the biphenyl molecule in the two stable positions. From [12].

single molecule. The most commonly used is to image the molecule with an STM before and after the electronic excitation and to examine the induced changes. Additional information on the molecular dynamics can be obtained by recording the tunnel current during the electronic excitation [12]. Some changes of the molecular configuration can thus be followed in real time. Of course, the time resolution (about 1 ms) is limited by the bandpass (about 1 kHz) of the tunnel current detection.

The first molecular dynamics induced by electronic excitation with an STM was the dissociation of a decaborane molecule adsorbed on a Si(111) surface [1]. The dissociation was monitored through the observation of molecular fragments on the surface. A threshold surface voltage around 4 V indicated that the excitation mechanism was indeed an electronic excitation. This study was followed by other examples of molecular dissociation through electronic excitation with an STM tip [43]. In a recent study, Sloan and Palmer [42] reported a two-electron dissociation mechanism that couples vibrational excitation and dissociative electron attachment steps.

As mentioned in section 2.1, the electronic excitation is able to deliver a large amount of energy to the molecule, to induce bond breaking and thus to lead to irreversible dynamical processes. This is especially true for electronic transitions (figures 1(c) and (d)). However, electron (hole) attachment (figures 1(a) and (b)) is able to deliver a smaller amount of energy provided the occupied and unoccupied molecular orbitals lie close in energy to the Fermi level of the surface. This has been observed to occur in the excitation of a biphenyl molecule adsorbed on a Si(100) surface [12]. In this case a bistable movement of the molecule between two stable configurations ( $S_1$  and  $S_2$ ) could be activated by hole attachment into occupied  $\pi$  resonances of the adsorbed biphenyl molecule (see figure 2). A bistable molecule is a very simple prototype of a molecular nanomachine. However, bistability is an interesting molecular

function since it can be used as molecular switches, molecular memories or molecular logic devices. At this point, we wish to emphasize that a molecular nanomachine is not simply a mechanical or an electronic device. As a molecule, it can show a very complex dynamical behaviour. This is illustrated by the bistable biphenyl case [12]. Indeed, in addition to the two stable ( $S_1$  and  $S_2$ ) states, a transient ( $T$ ) state has been observed to play an important role. This led us to demonstrate a new method for controlling the dynamics of a single molecule based on the localization of the electronic excitation inside the molecule [12]. It has been shown that different electronic resonances had different energies and were localized at different positions inside the biphenyl molecule. It was then possible to locally excite with an STM tip each of these resonances and to demonstrate that each resonance was associated to a given movement of the molecule, i.e. either the  $S_1 \rightarrow S_2$  switch or the  $S_1 \rightarrow T$  transition. From these results, the localization of the electronic excitation inside the molecule is manifestly a powerful parameter for controlling the dynamics of a single molecule.

#### 4. Conclusions and perspectives

The electronic processes for the excitation of individual atoms and molecules which have been discussed in this paper are still poorly understood. The main reason is the lack of experimental data on the electronic structure of adsorbed atoms and molecules. Further photoemission and inverse photoemission studies will be necessary to elucidate the structure of both their occupied and unoccupied electronic states. We wish also to emphasize that the electric field between the STM tip and the surface may strongly modify the energies of the electronic states of adsorbed atoms and molecules relative to the Fermi level of the surface, especially for semiconductor surfaces. Sophisticated simulations of these electric field induced effects are now available [27] and should contribute to a detailed description of the electronic structure of adsorbates under an STM tip.

In most of the cases that we have reviewed in this paper, the yield of the electronic processes (probability per electron for inducing a given process) is in the range  $10^{-6}$ – $10^{-10}$ . Increasing the yield would require being able to electronically decouple the atom or molecule from the substrate. This can be done either by using thin insulating layers [33, 44], wide band gap semiconductors [45], physisorbed rather than chemisorbed species [46], or passivated semiconductor surfaces [47, 48]. However, by doing so, the interactions between adsorbed nano-objects and the surface are decreased and the nano-objects can easily diffuse across the surface. This may prevent them from being efficiently excited electronically with an STM tip.

So far, the STM tip has been the main tool for activating the functions of individual nano-objects through their electronic excitation. Although the STM tip has enabled experimental studies on prototypes of molecular nanomachines, it has obvious limitations. Only relatively small molecular nano-objects having a size of a few nanometres [48] can be studied by this method. Furthermore, the electronic processes under the STM tip are difficult to control fully. To overcome these difficulties, other tools may be used such as the atomic force microscope (AFM) with a conducting tip for studying larger molecular assemblies or the scanning near field optical microscope (SNOM) for even larger nano-objects. Combining laser excitation with an STM [34] or AFM would also be another way to improve the control on the electronic processes.

So far the atoms and molecules used in such experiments for testing molecular nanomachines have been relatively simple. More complex functions at the molecular level will require the use of larger and more sophisticated assemblies of molecules and other kinds of nano-object. Molecules having specific functions can be designed [2]. Carbon nanotubes or semiconductor nanocrystals can be functionalized by the surrounding molecules [48]. The future certainly lies in combining these various nano-objects into specific architectures.



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## References

- [1] Dujardin G, Walkup R E and Avouris P 1992 *Science* **255** 1232
- [2] Joachim C, Gimzewski J K and Aviram A 2000 *Nature* **408** 541
- [3] Stoddart J F 2001 *Acc. Chem. Res.* **34** 411
- [4] Noji *et al* 1997 *Nature* **386** 299
- [5] Charron E, Giusti-Suzor A and Mies F H 1995 *J. Chem. Phys.* **103** 7359
- [6] Betzig E and Trautman J K 1992 *Science* **199** 189
- [7] Moerner W E and Orrit M 1999 *Science* **283** 1670
- [8] Feenstra R M 1994 *Surf. Sci.* **300** 965
- [9] Lorente N, Persson M, Lauhon L J and Ho W 2001 *Phys. Rev. Lett.* **86** 3694
- [10] Komeda T 2005 *Prog. Surf. Sci.* **78** 41
- [11] Eigler D M and Schweizer E K 1990 *Nature* **344** 524
- [12] Lastapis M, Martin M, Riedel D, Hellner L, Comtet G and Dujardin G 2005 *Science* **308** 1000
- [13] Berkovitz J 1979 *Photoabsorption, Photoionization and Photoelectron Spectroscopy* (New York: Academic)
- [14] Martin M M and Hynes J T 2004 *Femtochemistry and Femtobiology* (Amsterdam: Elsevier)
- [15] Schwentner N, Koch E E and Jortner J 1985 *Electronic Excitations in Condensed Rare Gases* vol 107 (Berlin: Springer)
- [16] Raseev G and Dujardin G 2003 *Proc. 9th Int. Workshop on Desorption Induced by Electronic Transitions* (Amsterdam: Elsevier) and articles therein
- [17] Kunz C 1979 *Synchrotron Radiation* vol 10 (Berlin: Springer)
- [18] Becker R S *et al* 1987 *Nature* **325** 419
- [19] Bartels L, Meyer G and Rieder K H 1997 *Phys. Rev. Lett.* **79** 697
- [20] Dujardin G *et al* 1998 *Phys. Rev. Lett.* **80** 3085
- [21] Brown D E *et al* 1998 *Science* **279** 542
- [22] Pascual J I *et al* 2003 *Nature* **423** 525
- [23] Comtet G *et al* 2004 *Phil. Trans. R. Soc. A* **362** 1217
- [24] Salam G P, Persson M and Palmer R E 1994 *Phys. Rev. B* **49** 10655
- [25] Smith N V 1988 *Rep. Prog. Phys.* **51** 1227
- [26] Lang *et al* 2000 *Phys. Rev. Lett.* **84** 979
- [27] Feenstra R M 2003 *J. Vac. Sci. Technol. B* **21** 2080
- [28] Klistner T, Becker R S and Vickers J S 1990 *Phys. Rev. B* **41** 3837
- [29] Shen T C *et al* 1995 *Science* **268** 1590
- [30] Soukiassian L *et al* 2003 *Phys. Rev. B* **68** 035303
- [31] Dujardin G *et al* 2001 *Phys. Rev. B* **63** 81305R
- [32] Bartels L *et al* 1999 *Chem. Phys. Lett.* **313** 53
- [33] Qiu X H, Nazin G V and Ho W 2003 *Science* **299** 542
- [34] Stokbro *et al* 1998 *Phys. Rev. Lett.* **80** 2618
- [35] Sloan P A, Hedouin M F G and Palmer R E 2003 *Phys. Rev. Lett.* **91** 118301
- [36] Vondrak T and Zhu X-Y 1999 *Phys. Rev. Lett.* **82** 1967
- [37] Riedel D, Mayne A J and Dujardin G 2005 *Phys. Rev. B* **72** 233304
- [38] Berndt R *et al* 1993 *Science* **262** 1425
- [39] Čavar E, Blüm M-C, Pivetta M, Patthey F, Chergui M and Schneider W-D 2005 *Phys. Rev. Lett.* **95** 196102
- [40] Soukiassian L, Mayne A J, Baffou G, Comtet G, Hellner L, Dujardin G and Gourdon A 2005 *J. Chem. Phys.* **122** 134704
- [41] Cranney M, Mayne A J, Comtet G and Dujardin G 2005 *Surf. Sci.* **593** 139
- [42] Sloan P A and Palmer R E 2005 *Nature* **434** 367
- [43] Ho W 2002 *J. Chem. Phys.* **117** 11033
- [44] Repp J, Meyer G, Olsson F E and Persson M 2004 *Science* **305** 493
- [45] Bobrov K, Mayne A J and Dujardin G 2001 *Nature* **413** 616
- [46] Carbone M *et al* 2003 *J. Phys.: Condens. Matter* **15** L327
- [47] Mayne A J, Soukiassian L, Commaux N, Comtet G and Dujardin G 2004 *Appl. Phys. Lett.* **85** 5380
- [48] Bernard R *et al* 2005 *Appl. Phys. Lett.* **87** 053114