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Observation of Organic Molecules by Scanning Tunneling Microscope

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Abstract

We have improved the conventional STM as regards the observation of organic molecules. To characterize this system, we observed liquid crystals. The molecules we chose as samples are n-alkylcyanobiphenyl (7CB and 8CB) absorbed on HOPG and MoS₂ substrates. STM images of 8CB on HOPG indicated that the molecules aligned to form periodic bilayer structures. As for 7CB on HOPG and MoS₂, monolayer structures were exhibited in each case. The results showed that both the anchoring effect (which is an interaction between sample and substrate) and the interaction of dipole moments affected the ordering of the molecules on the substrate. The images obtained using our system were then compared with previous experimental results.

1. Introduction

For atomic and molecular scale surface scientific studies, the scanning tunneling microscope (STM) is an attractive tool. It allows us direct observation of surface contours of electron wave functions on an atomic scale, revealing important information on the ordering of surface atoms and molecules, as well as their absorbed states. Since Binnig and Rohrer showed the potential of the STM in 1982⁽¹⁾, an enormous number of specimens have been observed with the STM, such as metal and semiconductor surfaces, absorbed atoms and molecules on these surfaces, and organic or biological molecules⁽²⁾.

The observation of molecules using the STM was thought to be difficult because of the low tunneling conductivity of molecules. However, a great many molecules (even biological molecules, such as a DNA) have been successfully observed⁽³⁾. Nevertheless many curious properties of molecule images taken by the STM, such as bias dependency⁽⁴⁾, are still not well understood. Hence many people in the fields of organic and molecular biology are interested in the STM and have began to use it.

We have been using various techniques to study molecular thin films, which show remarkable electronic and optical properties. For example, we have measured molecular dynamics with time-resolved fluorescence depolarization⁽⁵⁾; we have used inelastic tunneling spectroscopy to observe the molecular vibration of molecules sandwiched between superconductive thin film electrodes⁽⁶⁾, and we have employed phase-contrast

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microscopes to characterize macroscopic properties such as domain formation of Langmuir Blodgett (LB) films⁽⁷⁾. In this paper, we are going to report on a new approach to the microscopic study of molecules using the STM.

As a first step of this study, we improved our conventional STM, making it suitable for molecular observation. Then we observed liquid crystals with the STM. The reason why we chose liquid crystals, as test samples is that they have been observed by others with molecule resolution⁽⁸⁾⁽⁹⁾. The liquid crystals deposited on the HOPG and MoS₂ substrates have particular orientation characteristics which depend upon the length of the alkyl tails and substrate surface characteristics. If one can obtain a clear image of the molecules of the liquid crystals with the STM, the other molecules such as LB thin films could be observed.

Smith et al. have studied n-alkylcyanobiphenyl (nCB) molecules deposited on graphite, and observed two-dimensional molecular ordering similar to that of nCB smectic bilayers⁽⁸⁾. Hara et al. have observed smectic liquid crystals (4'-n-octyl-4-cyanobiphenyl: 8CB) on a MoS₂ substrate⁽¹⁰⁾. They have studied the STM image of the liquid crystals with various n's⁽¹¹⁾.

We report here on the STM image of 8CB on both HOPG and MoS₂ as well as the image of 7CB on MoS₂ obtained by our improved STM. Our results are then compared with previous ones to confirm our STM capabilities.

2. Instrumentation

To observe organic molecules such as liquid crystals by means of the STM, it is necessary to detect rather small tunneling currents with good stability (the current noise level must be less than 10 pA). We improved the commercial instrument SAM3000: Seiko Scientific Instrument for this experiment.

Tunneling current is detected by a high gain I-V converter and changed to voltage signal. For small current detection, we had to design an appropriate converter. Figure 1 is a circuit diagram of the high gain (10^9 V/A), low noise (less than 10 pA_{p-p}) converter which we have designed. Careful attention was needed to reduce the noise. A Teflon insulator pad and low noise cable (Junkousya DFS series) were employed.

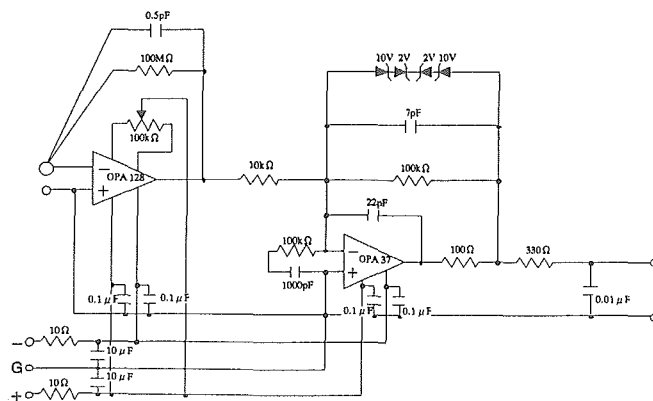


Fig. 1: Circuit Diagram of Tunneling Current to Voltage Converter.

The cut-off frequency of this converter is 1.3 kHz, which is rather low for the constant current mode of the STM, but which is enough for constant height mode. The latter was used in this experiment.

To reduce the high frequency noise of the converter, a 4th order low pass filter (NF-SRL4B12) was inserted just after the converter. Both the converter and the filter are driven with batteries to avoid noise from power lines. Since a constant voltage circuit stabilizing output of the batteries was not used, it was necessary to adjust the offset of these circuits each time batteries were changed.

The cut-off frequency of the feedback circuit was limited to 30 kHz by the insertion of appropriate capacitors to the circuit board to realize good signal to noise ratio, but at the sacrifice of response time. Since instability of the high voltage amplifiers used to drive the piezo actuators would have disturbed the molecular imaging, a low pass filter composed of passive R-C circuits was attached to the output of the amplifiers. Not only the stability of the amplifier for the z direction but also of the amplifiers for the x and y directions are important.

To reduce the noise originating from the ground loops, a well-separated ground between the digital circuits and the analog circuits is used and connected to the ground point of the converter.

The sample holding stage of the STM is made of Macor, which is a good insulator for low leakage current.

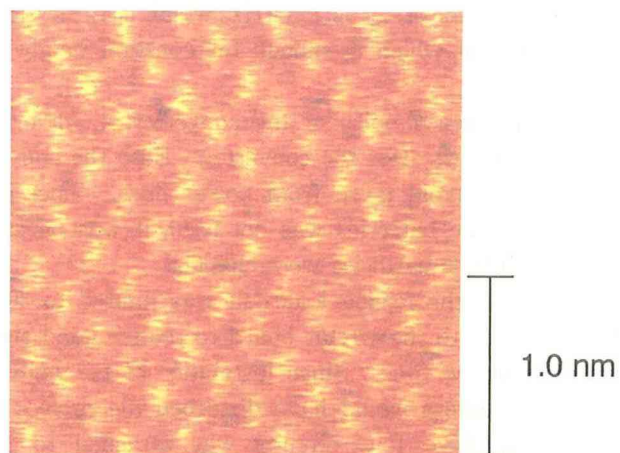
3. Sample preparations

3. 1 Substrates

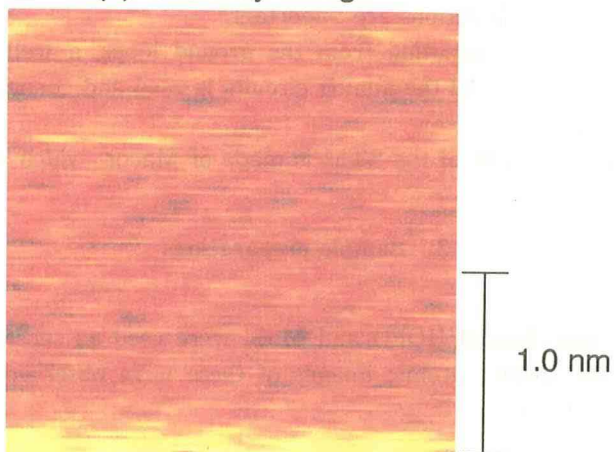
In our experiment cleaved HOPG and MoS₂ were used as substrates. To characterize the substrates, surface atomic images of these were observed before depositing the sample on their surfaces.

3. 1. 1 HOPG

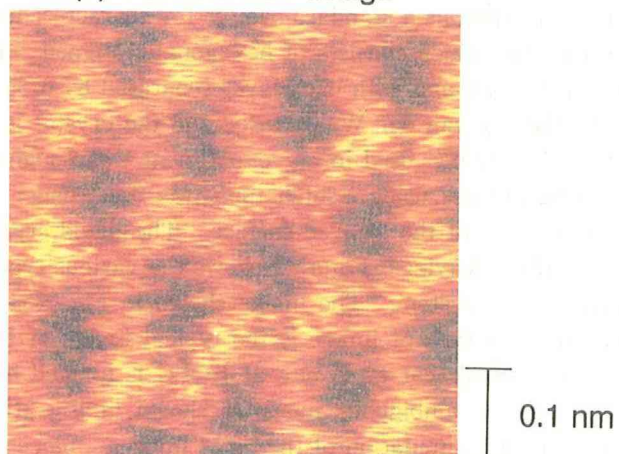
HOPG was commonly used as a standard sample for characterizing the STM in air. HOPG is a layered material which consists of hexagonally aligned carbon atoms separated 0.142 nm from each other and with each layer separated by 0.355 nm. Each layer is bonded with each other by van der Waals force and the crystal is easily cleaved to make clean surfaces. The HOPG used in our experiment was bought from Union Carbide, Inc. The cleaving process using Scotch tape was done under an optical microscope to check the roughness of the cleaved surface. The liquid crystals were deposited as soon as possible after cleaving. Figure 2 shows the various types of image of the HOPG surface taken by our system. The image shown in Fig.2(a) is one commonly taken in the system and this type of image is the typical image of HOPG observed in air. It is generally understood that an A site of HOPG is imaged brighter than its B site. With undesired tips, an ambiguous image is shown in Fig.2(b). That is A in accordance with the computer simulation of the STM images. Since the STM image is sensitive to the atomic structure of the tip apex, analyzing the images taken of cleaved surface is only one way to characterize the tip of the STM in air. All of the tips used in this experiment were checked to determine whether the appropriate image of the



(a) Ordinary Image



(b) Ribbon like Image



(c) Honeycomb like Image

Fig. 2: STM Images of HOPG

cleaved surface could be obtained with them before observing the molecule.

In vacuum, when absorbed oxygen is removed from a surface, a different surface structure image is obtained, i. e. a honeycomb structure of surface atoms. Even in air, there have been instance where we obtained the same image as shown in Fig. 2(c). The STM image depends on not only the tip apex structure but also on the conditions of the sample's surface.

3. 1. 2 MoS₂

MoS₂ is also a layered material, It is naturally produced, and used as a tribological lubricant. MoS₂ is a typical layered transition-metal dichalcogenide, which forms the sandwich structure S-Mo-S. Each layer of this structure is bonded with its adjacent layers by the van der Waals force. In a cleaved surface the sulfur atoms form a hex-

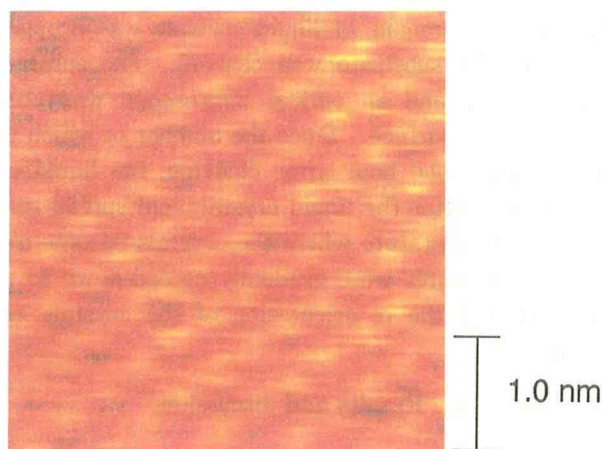


Fig. 3: STM Images of MoS₂
Cleaved Surface

agonal lattice. In this surface, the separation between sulfur atoms is 0.316 nm. The distance between the layers is 0.298 nm. Since there are no dangling bonds on its cleaved surface, the surface is considered to be stable. One of the differences between the HOPG and the MoS₂ substrates is that MoS₂ has a polarity because of the higher ionicity of the S-Mo bonds. The difference may cause the difference in adsorbed structures between the HOPG and MoS₂. It follows that different images of the same sample on these substrates are to be expected.

Figure 3 is an STM image of a MoS₂ cleaved surface. The bright spots in the image are the sulfur atoms, and the relatively darker spot surrounded by the bright spots, is the Mo atom. The MoS₂ used in this study is a natural crystal from Quebec, Canada (Ward's Natural Science Inc.).

Because MoS₂ is a semiconductor, atomic images of the surface can be taken in regions of restricted bias. The band structure of a surface affects tunneling current. Hence it is necessary to pay special attention to bias dependency when one wishes to understand the imaging mechanism of molecules.

3. 2 Samples (Liquid Crystals)

In our experiment, we used 8CB and 7CB as samples. These liquid crystals are 4'-n-alkyl-4-cyanobiphenyl (mCB, where m=7, 8, is the number of carbons in the alkyl group). We have chosen two different substrates to distinguish the effects of substrate properties. Furthermore we employed two different samples to investigate the effect of sample structure on orientation of the molecules.

The samples for the STM study were prepared in the following way.

- (1) cleaving of the substrate (HOPG and MoS₂)
- (2) dropping the liquid crystals on the substrates
- (3) heating the substrates
- (4) allowing the substrates to cooldown to room temperature

In each procedure a small amount of liquid crystals was dropped on a substrates with a micro-syringe after the substrate was cleaved. The substrate was thoroughly with moistured liquid crystals, and an optical microscope was used to observe the spreading of the crystals on the surface. Since the manner in which the crystals spread begins to differ approximately one hour after cleaving, the liquid crystals had to be dropped as soon as possible. After the liquid crystals had spread sufficiently, the substrates were heated up to a temperature where the crystals become a isotropic liquid (5 min. at 60C). Then the substrates were gradually cooled down to room temperature. This heating process promoted the re-orientation of the crystals and therefore good images could be obtained.

4. Results and discussion

All our experiments were done at room temperature and in air. The images of the molecules which we observed were variable current images. The bright spots in the images corresponded to those places where high tunneling conductivity was observed. We used Pt-Ir (90%-10%) alloyed tips as probes. These probes were made from polycrystalline wire using a nipper.

4. 1 8CB on HOPG

An STM image of 8CB molecules on HOPG is shown in Fig. 4(a). The tip bias was set to 1.2V and the feedback tunneling current was 0.2 nA. STM images of the π orbital can be observed as brighter spots than those of the σ orbital, because the π electrons are bound less weakly than σ electrons; moreover the electron wave function of the former electrons interact well with those of the tips. Fig. 4(a) shows that 8CB on HOPG exhibited a periodic bilayer structure in which cyanobiphenyl head groups aligned face to face and 8 molecules of 8CB formed a unit cell. Though bulk 8CB has a smectic bilayer structure, the structure of 8CB in the adsorbed state is slightly different from it. The alkyl chain of each molecule aligned along a graphite lattice vector and cyano groups aligned along a different vector, one rotated by an angle of 60 degrees. This was caused by the anchoring effect in which the hydrogen orbitals of n-alkanes fit into the holes in the (0001) plane of the graphite. These results were basi-

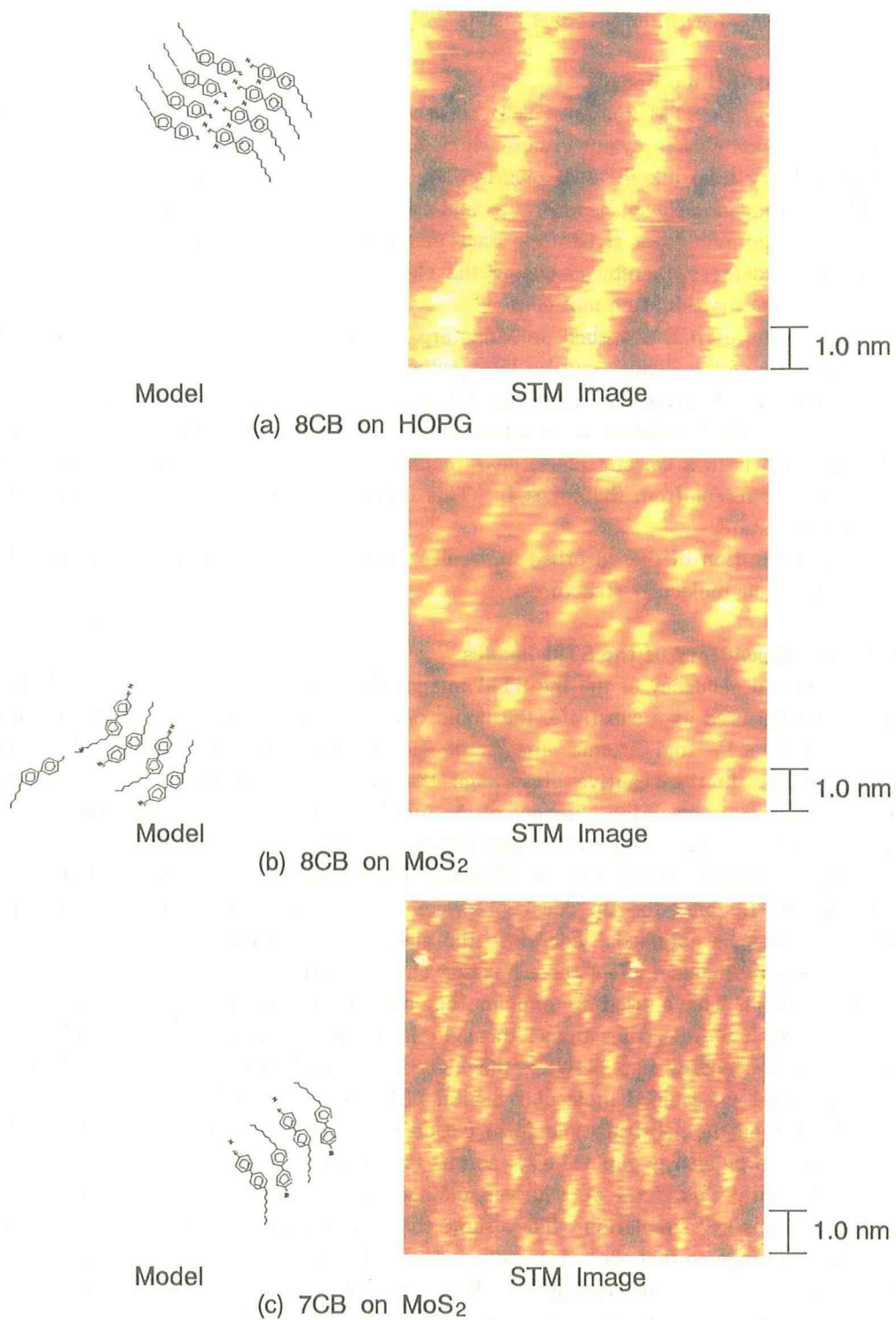


Fig. 4: STM Images and Intuitive Models of Absorbed Molecule (8CB on HOPG, 8CB on MoS₂, 7CB on MoS₂)

cally in agreement with the previous results⁽⁸⁾⁽¹⁰⁾⁽¹¹⁾⁽¹²⁾.

4. 2 8CB and 7CB on MoS₂

Fig. 4(b) is an STM image of 8CB adsorbed on MoS₂. In this image, the bright spot corresponds also to cyano groups which have π electrons that have higher tunneling probability than alken. 8CB on MoS₂ exhibited different structure from that on HOPG. The cyanobiphenyl head groups and the alkyl tails alternate in each row, and form a periodic monolayer structure. Each unit cell is symmetric under rotation by an angle of 180 degrees, thereby canceling the electric dipole moments of the molecules which take place within each unit cell.

The results of 7CB adsorbed on MoS₂ are shown in Fig. 4(c). If we assume that the brightness of the images can be interpreted as previously discussed, the molecules align in the way shown on the right side of Fig. 4(c). 7CB on MoS₂ is similar in structure to 8CB, which exhibits a structure that is different from that in bulk state. Although 7CB is in a smectic phase near room temperature, as is 8CB, its molecular structure is different from that of 8CB. This difference in molecular structure affects the adsorbed state.

The orientation of the adsorbed molecules varied with the differences of the substrates and their molecular structures.

4. 3 Bias dependency of the STM images.

The bias dependency of the the STM images shown in Fig. 4 was observed. In the case of HOPG used as a substrate, the liquid crystals could be observed in the tip bias range above +1V and atomic images of HOPG substrates were observed below about +0.1V. In the negative bias range, the same bias dependency was observed. When the substrate was MoS₂, images of the molecules below -1.2V were obtained. In the positive bias range (0 to +3V), only substrate images were observed.

Since molecular images can be obtained after imaging the substrate atoms and resuming the tip bias, the tip does not sweep out the adsorbed molecules when the substrate image is obtained. Therefore the electronic structure of the molecules and the tunneling mechanism affect these imaging characteristics.

Hara et al.⁽¹⁰⁾ have tried to explain this phenomenon with a resonant tunneling model in which the electrons tunnel through the molecule energy levels. Nejoh⁽⁴⁾ has shown that the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is reduced when the molecules are adsorbed on the substrate and form periodic crystal structures, and that the 8CB, which has a large energy gap (11 eV), can be visualized by a tunneling bias around 800 mV. Recently Tukada et al.⁽¹³⁾ have explained the imaging properties of benzene on HOPG by computer simulation. They show that the molecule becomes transparent in the low bias range so that the substrate is visualized through the molecule, and that the wave function of electrons coming from HOPG do not contain the components of wave functions of benzene in the low bias range.

The above discussions show that the STM has the potential to make image of various

kinds of molecules.

5. Conclusion

We have improved our conventional STM system operating in air, with which organic molecules absorbed on HOPG and MoS₂ were observed. We obtained bilayer structures of 8CB on HOPG and monolayer structures of 7CB on MoS₂. The previous results of other groups were confirmed and it was shown that our system is capable for imaging molecules.

With this improved system, we plan to observe other organic thin films such as LB films. Although we have obtained ambiguous images of arachidic acid on MoS₂ formed by the LB method, to clarify to what structure the images corresponds, further investigations are needed.

Acknowledgments

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