Atomic-scale rectification at microwave frequency

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(Received 12 September 2005; accepted 29 November 2005; published online 12 January 2006)

Microwave of known amplitude and frequency, irradiating the junction of a low temperature scanning tunneling microscope, was found to induce a dc signal. This rectification current is spatially localized and exhibits chemical sensitivity at the atomic scale. Dependence of the rectification current on the sample bias voltage reveals spin splitting in the electronic state of a single Mn atom and vibrations of single MnCO molecule. These results demonstrate the feasibility of atomic scale nonlinear spectroscopy and the potential for the detection of resonance phenomena excited with a spatially extended electromagnetic wave. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159491]

Rectification, the change from ac to dc, is a well-known effect in electronics. Rectifying diode is one of the fundamental components in analog and digital electronics. Molecular rectifier was first proposed by Aviram and Ratner in 1974.[1] Since then, intense effort has been invested toward the realization of such molecular rectifiers.[2] Interestingly, carbon nanotubes and silicon nanowires also exhibited rectifying properties when they had defects[3] or junctions.[4,5] The rectifying properties of these molecules, nanotubes, and nanowires are manifested as asymmetric current-voltage (I-V) curves. However, no direct measurement of the rectification current associated with single molecules has been reported.

Here we present quantitative results of rectification current from single adsorbed atoms and molecules due to microwave irradiation of the scanning tunneling microscope (STM) junction. It was suggested in 1987 that laser-rectification in STM could be used to measure the tunneling time.[6] Two years later, preliminary results were reported, and a tunneling time was derived.[7] In retrospect, the dc current induced by 1.06 μm laser irradiation of a silicon sample was most likely due to the surface photovoltage effect.[8,9] In 1990, Kuk and co-workers observed small variations in laser-induced surface photovoltage on Si(111)-7×7 with STM and tentatively attributed it to rectification.[9] Two years later, with improved instrumentation, Kochanski and Bell found that the small variations were systematic errors.[10] Also in the early 1990's, the Walther group reported STM observation of rectification current induced by 9.3 μm laser.[11–13] However, in a recent study using 1.3 μm laser, Walther and co-workers concluded that the laser-induced dc current was dominated by thermocurrent.[14] The study of rectification induced by 670 nm laser also found that the data contained substantial thermal contribution.[15] In addition to rectification, the nonlinearity of the STM junction also leads to the generation of higher harmonics,[16–20] as well as the difference and sum frequencies (mixing).[11–14,21,22]

In this paper, the rectification current was measured from single Mn atoms and MnCO molecules adsorbed on NiAl(110). The NiAl(110) surface and W probe tips were cleaned by Ne^+ sputtering and annealing in ultrahigh vacuum. Low coverages of Mn atoms were evaporated onto the sample at 18 K, followed by CO dosage. Some CO molecules are bonded to the adsorbed Mn atoms to form MnCO.[23]

The experimental arrangement is shown schematically in Fig. 1. The continuous wave microwave from a generator was first amplified (+41 dB), and then fed into a directional coupler. The reflected wave was monitored by an oscilloscope and minimized by adjusting the stub tuner. A square wave from the function generator modulated the microwave before the radiation was delivered to the STM junction via a two-turn coil. A lock-in amplifier was used to detect the change in the dc tunneling current induced by the microwave. Inset 1 (circle) shows a zoom-in view of the coil, tip, and sample. Inset 2 (rectangle) shows the time traces of the dc tunneling current (upper trace) and the control voltage (lower trace) measured simultaneously on a Mn atom with the feedback turned off. The amplitude of the microwave signal from the generator was V_{IN}=5 mV (rms value, similarly for V_J and V_M introduced below), at a frequency of 800 MHz.[24] The amplified microwave was amplitude modulated by turning it on and off with the control voltage at a frequency of 200 Hz. The dc tunneling current is modulated with an added square wave component and assumes two levels: 1.0 nA when microwave is off (control=0 V) and 1.2 nA when microwave is on (control=5 V).

There are two possible origins of this increase in dc tunneling current with microwave irradiation: rectification versus thermal effects. The microwave with V_{IN}=5 mV caused a temperature increase of about 25 mK as measured with a Si diode attached to the STM, and a noticeable thermal drift. To minimize thermal contribution, the data were measured after

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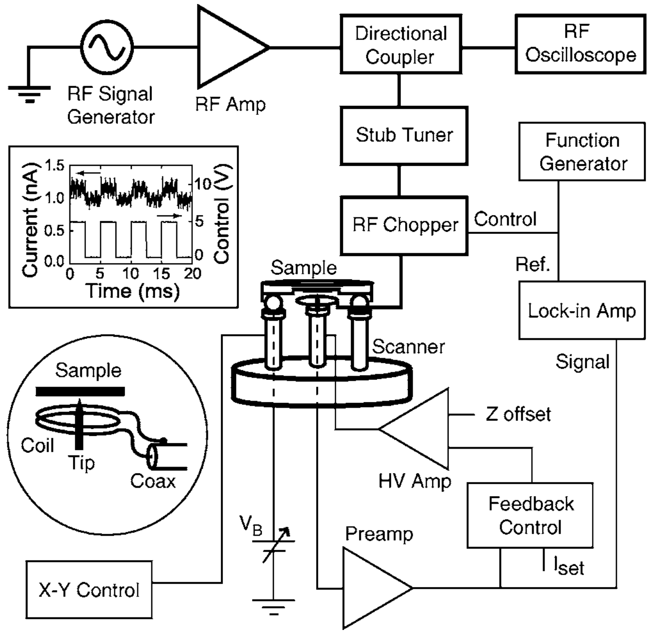

FIG. 1. Schematic of the experimental setup. The STM scanner and sample are drawn in the center. Conventional STM electronics are drawn below in thin lines, while microwave electronics are drawn above in thick lines. Inset 1 (circle) shows a zoom-in view of the coil, tip, and sample. Inset 2 (square) shows tunneling current (upper trace) and control voltage (lower trace) measured simultaneously with tip above a Mn atom and feedback turned off. The gap was set at (1.0 nA, +1.87 V); input microwave was V_{IN}=5 mV at 800 MHz.

the temperature had equilibrated to a new steady state and the drift had subsided. We observed strong spatial dependence of the difference between the two current levels: as soon as the STM tip was moved away from the Mn atom, the

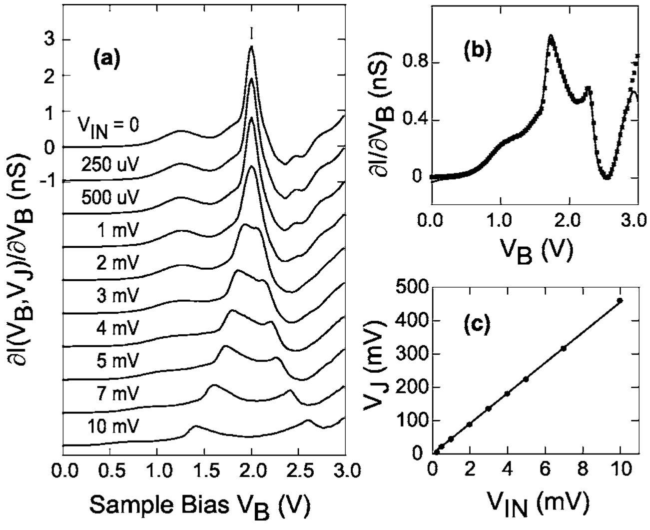

FIG. 2. (a) Differential conductance spectra of a single Mn atom adsorbed on NiAl(110) surface with constant microwave input (no amplitude modulation). The lock-in amplifier was configured to provide a sample bias modulation of V_M=10 mV at 200 Hz, and measure the first harmonic in the tunneling current to yield $\partial I(V_B,V_J)/\partial V_B$. As V_{IN} was increased, the peak at 2.0 V became broadened and eventually split into two. **(b)** The spectrum with V_{IN}=5 mV was fitted numerically (line) to extract V_J, the microwave amplitude across the STM junction. The deviations at both ends, V_B=0 and V_B=3.0 V, are caused by extrapolation of the measured spectrum to outside the interval (0, 3.0 V). **(c)** Plot of extracted V_J vs V_{IN}. The line is a linear fit with the constraint of zero intercept, which yields $V_J = 45.5 \times V_{IN}$.

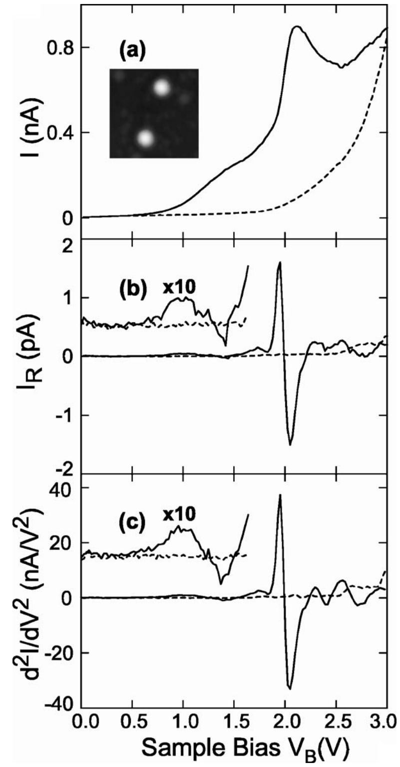

FIG. 3. (a) The solid line (dashed line) shows I-V characteristics measured on (off) a single Mn atom adsorbed on the NiAl(110) surface. Inset shows an STM image of two such Mn atoms: image size is 6.25×6.25 nm^2, tunneling condition is 1.0 nA at 1.80 V. **(b)** The solid line (dashed line) shows rectification current I_R as a function of V_B measured on (off) a Mn atom. These two spectra were taken with microwave amplitude V_{IN}=220 μV (so that V_J=10.0 mV) and chopping frequency of 200 Hz. **(c)** d^2I/dV^2 spectra measured on (solid line) and off (dashed line) the same Mn atom. These two spectra were taken with no microwave input. The lock-in amplifier supplied the sample bias modulation of V_M=10 mV at 200 Hz and detected the second harmonic in the tunneling current.

current difference disappeared. Furthermore, this current difference was sensitive to the sample bias. The current with the microwave on could even be made less than that with the microwave off by tuning the sample bias. These spatial and sample bias dependences are difficult to explain by thermal effects. In contrast, they can be accounted for by the rectification current caused by a single adsorbed Mn atom (see Fig. 3 and explanation below).

A quantitative analysis of the rectification current requires a calibration of the microwave amplitude in the junction. The total sample bias is $V_B + \sqrt{2}V_J \cos(\omega t)$, where V_B is the applied dc sample bias and V_J is the rms amplitude of the induced voltage difference between the tip and the sample at the microwave frequency $\omega/2\pi$=800 MHz.[24] Electron tunneling is a very fast quantum mechanical process, with estimated traversal time on the order of 10^{-15} second across the STM junction.[25] In the present experiment, using microwave below 2 GHz, the tunneling current is expected to follow changes in the total sample bias and becomes time-dependent. The current preamplifier, however, has a bandwidth of 4 kHz and thus filters out signals at 800 MHz and all higher harmonics. Its output is dc, corresponding to the time-averaged tunneling current:

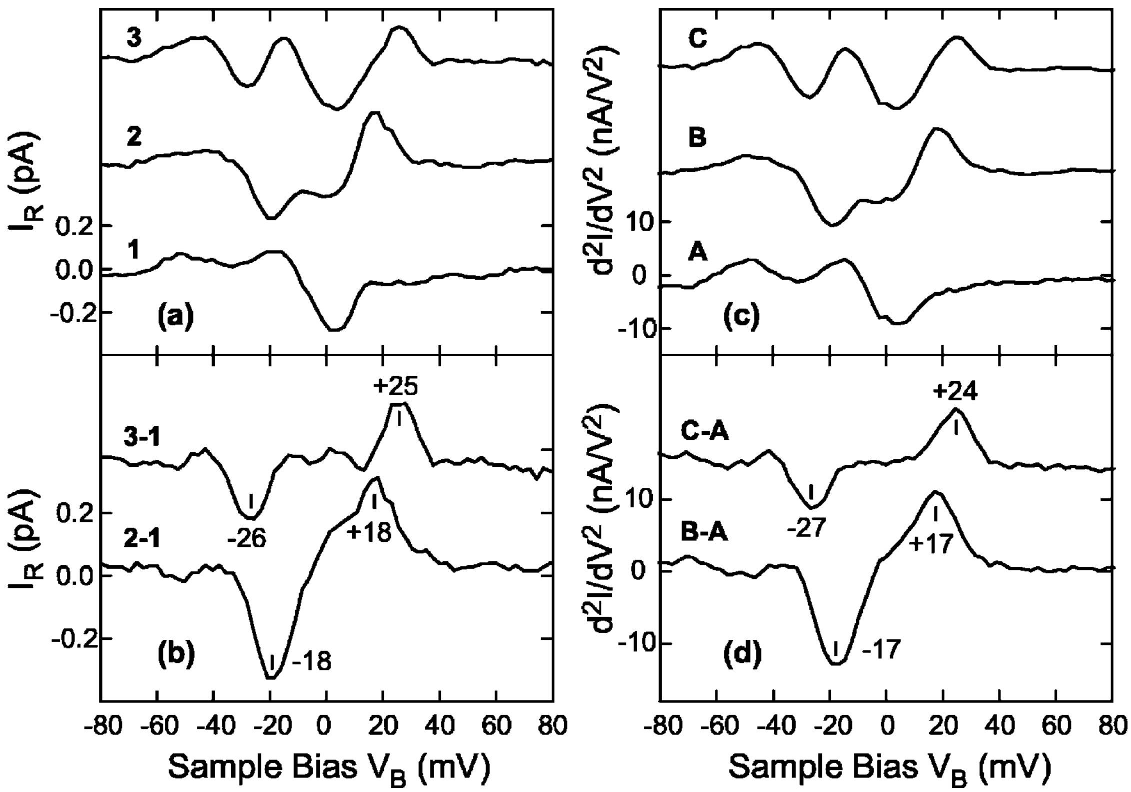

FIG. 4. (a) Rectification spectra measured off (curve 1) and on (curves 2 and 3) two different MnCO species adsorbed on NiAl(110). These three spectra were measured with the microwave amplitude V_{IN}=154 μV (corresponding to V_J=7.0 mV) and chopping frequency of 200 Hz. Every curve was averaged over 10 scans of 42 sec each. **(b)** Background subtracted rectification spectra in (a), revealing different energies of the hindered CO rotation mode: 18 meV and 25.5 meV. **(c)** d^2I/dV^2 spectra measured off (curve A) and on (curves B and C) the same two MnCO species with no microwave input.[28] These three spectra were measured with the sample bias modulation of V_M=7 mV at 200 Hz. Curve A (B, C) was averaged over 10 (12, 10) scans of 42 sec each. **(d)** Background subtracted d^2I/dV^2 spectra in (c), showing the same hindered CO rotation modes as seen in (b).

$$I(V_B,V_J) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} I[V_B + \sqrt{2}V_J\cos(\omega t)]dt. \quad (1)$$

The function in the integrand, $I(V)$, has the same form as the static I-V characteristics measured in the absence of microwave, but with a time dependent argument. This provided a method of calibration. The measured $\partial I(V_B,V_J)/\partial V_B$ spectra for a single Mn atom adsorbed on NiAl(110) for different V_{IN} and without amplitude modulation are shown in Fig. 2(a). In the absence of microwave (V_{IN}=0), the $\partial I(V_B,V_J)/\partial V_B$ spectrum is equivalent to dI/dV and has a narrow peak at 2.0 V and a broad peak at 1.3 V, associated with the spin splitting of Mn *sp* states from magnetic interaction with its *d* electrons.[26] As V_{IN} is increased, the peak at 2.0 V becomes broader and eventually splits into two. This splitting is due to rectification of the microwave in the junction. Figure 2(b) shows the measured data and the fit (line) following Eq. (1) for V_{IN}=5 mV, from which the corresponding V_J can be extracted. Similar fitting agreement is obtained for the other spectra. A plot of the extracted V_J versus V_{IN} is shown in Fig. 2(c), yielding a slope 45.5 from the best linear fit.[27]

The sample bias dependence of the rectification current is compared with the d^2I/dV^2 spectra taken under equivalent conditions. Because of the small amplitude of microwave, the resulting temperature increase was within several mK. Thermal drift was negligible, and the results do not contain thermal contributions. In Fig. 3(a), an STM image with two Mn atoms is shown (inset) as well as the I-V characteristics measured on (solid line) and off (dashed line) a Mn atom. The corresponding rectification and d^2I/dV^2 spectra are shown in Figs. 3(b) and 3(c), respectively. We can see in Fig. 3(b) that the rectification spectra measured on and off the adsorbed Mn atom are distinctly different, demonstrating that the rectification process retains the high spatial resolution of STM, despite the spatially extended microwave radiation. We can also see that the rectification spectrum of a single Mn atom follows closely the d^2I/dV^2 spectrum, including the fine structures.

The explanation for the rectification current following d^2I/dV^2 signal is contained in Eq. (1). In the limit of small V_J, a Taylor series expansion of the integrand about V_B can be carried out. The integration up to the second order in V_J yields

$$I(V_B,V_J) = I(V_B) + I_R(V_B,V_J) \cong I(V_B) + \frac{V_J^2}{2}\frac{d^2I}{dV^2}(V_B). \quad (2)$$

It follows from Eq. (2) that the leading term for the rectification current I_R is proportional to d^2I/dV^2. If d^2I/dV^2 is greater (smaller) than zero at certain sample bias, then the rectification current is positive (negative), showing the possible sign change in I_R. The peak value of d^2I/dV^2 in Fig. 3(c) is 37.4 nA/V^2, yielding 1.87 pA for the peak of the rectification current, in good agreement with the measured value of 1.61 pA in Fig. 3(b). Note that the rectification current and the d^2I/dV^2 spectrum were measured independently. The fact that they quantitatively agree with each other confirms the identification of the microwave-induced dc current as the rectification current and the validity of our analysis. In addition, we have verified experimentally that I_R scales with V_J^2 over the range of V_J from 0 to 50 mV.

The rectification spectra measured off (curve 1) and on (curves 2 and 3) two different MnCO molecules are shown in Fig. 4(a). In Fig. 4(b), the background NiAl(110) spectrum has been subtracted from the two MnCO spectra. The corresponding d^2I/dV^2 spectra measured off (curve a) and on (curves b and c) the same MnCO molecules and the background-subtracted d^2I/dV^2 spectra are shown in Figs. 4(c) and 4(d), respectively.[28] It can be seen that the rectification spectra and d^2I/dV^2 spectra quantitatively agree with each other. In Figs. 4(b) and 4(d), the peaks occur at essentially the same bias voltages (the spectra were obtained with 2.5 mV steps). The d^2I/dV^2 spectrum has been shown to be sensitive to inelastic electron tunneling and peaks appear when the tunneling electrons have energy equal to that of an active vibrational mode of the molecule in the junction.[29] These results demonstrate that the rectification current is sensitive to inelastic electron tunneling through a single molecule.

We note that, in the present experiment, the information revealed by the rectification current is identical to that in the conventional d^2I/dV^2 spectrum. However, in other phenomena such as electron spin resonance, changes are expected in the rectification current associated with microwave absorption. Since such changes are likely to be small, quantitative understanding of the rectification current in the present nonresonance case will prove crucial in the identification of those small changes.

In conclusion, microwave irradiating the STM junction gives rise to an electric field in the junction and a corresponding voltage difference between the tip and the atom or molecule on the surface. The adsorbed species is driven by this induced field and voltage, leading to a rectified dc current that reflects the intrinsic properties of the adsorbed atom or molecule, and in the present experiments, the spin split atomic electronic states and molecular vibrations. These results represent the first direct, quantitative measurement of the rectification current due to single atoms and molecules.

This material is based on work supported by the National Science Foundation under Grant No. 0102887. J.H.L. is additionally supported by the BK21 Project. We have benefited from H. J. Lee, J. Marohn, and P. J. Burke in the implementation of the microwave techniques.

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[2] For a recent review, see R. M. Metzger, Chem. Rev. (Washington, D.C.) **103**, 3803 (2003).
[3] P. G. Collins, A. Zettl, H. Bando, A. Thess, and R. E. Smalley, Science **278**, 100 (1997).
[4] J. Hu, M. Ouyang, P. Yang, and C. M. Lieber, Nature (London) **399**, 48 (1999).
[5] Z. Yao, H. W. CH. Postma, L. Balents, and C. Dekker, Nature (London) **402**, 273 (1999).
[6] P. H. Cutler, T. E. Feuchtwang, T. T. Tsong, Y. Kuk, H. Nguyen, and A. A. Lucas, Phys. Rev. B **35**, 7774 (1987).
[7] H. Q. Nguyen, P. H. Cutler, T. E. Feuchtwang, Z.-H. Huang, Y. Kuk, P. J. Silverman, A. A. Lucas, and T. E. Sullivan, IEEE Trans. Electron Devices **36**, 2671 (1989).
[8] R. J. Hamers and K. Markert, Phys. Rev. Lett. **64**, 1051 (1990).
[9] Y. Kuk, R. S. Becker, P. J. Silverman, and G. P. Kochanski, Phys. Rev. Lett. **65**, 456 (1990).
[10] G. P. Kochanski and R. F. Bell, Surf. Sci. **273**, L435 (1992).
[11] W. Krieger, T. Suzuki, M. Völcker, and H. Walther, Phys. Rev. B **41**, 10229 (1990).
[12] M. Völcker, W. Krieger, T. Suzuki, and H. Walther, J. Vac. Sci. Technol. B **9**, 541 (1991).
[13] M. Volcker, W. Krieger, and H. Walther, Phys. Rev. Lett. **66**, 1717 (1991).
[14] Th. Gutjahr-Löser, A. Hornsteiner, W. Krieger, and H. Walther, J. Appl. Phys. **85**, 6331 (1999).
[15] A. V. Bragas, S. M. Landi, and O. E. Martinez, Appl. Phys. Lett. **72**, 2075 (1998).
[16] G. P. Kochanski, Phys. Rev. Lett. **62**, 2285 (1989).
[17] B. Michel, W. Mizutani, R. Schierle, A. Jarosch, W. Knop, H. Benedickter, W. Bächtold, and H. Rohrer, Rev. Sci. Instrum. **63**, 4080 (1992).
[18] W. Seifert, E. Gerner, M. Stachel, and K. Dransfeld, Ultramicroscopy **42**, 379 (1992).
[19] S. J. Stranick and P. S. Weiss, J. Phys. Chem. **98**, 1762 (1994).
[20] J.-P. Bourgoin, M. B. Johnson, and B. Michel, Appl. Phys. Lett. **65**, 2045 (1994).
[21] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, Science **271**, 1705 (1996).
[22] J. Schmidt, D. H. Rapoport, and H. J. Frohlich, Rev. Sci. Instrum. **70**, 3377 (1999).
[23] H. J. Lee, Ph.D. thesis, Cornell University, 2004.
[24] All the data presented in this paper were obtained at 800 MHz. The same phenomena were also observed at 1.3 GHz. No resonance effects were apparent in the present experiments.
[25] R. Wiesendanger, *Scanning Probe Microscopy and Spectroscopy* (Cambridge University Press, Cambridge, 1994), pp. 34-35.
[26] H. J. Lee, W. Ho, and M. Persson, Phys. Rev. Lett. **92**, 186802 (2004).
[27] This experimentally derived amplification of 45.5 for 800 MHz microwave differs by less than 4% for three experimental runs with different W tips (45.9, 45.5, 43.7). For 1.3 GHz microwave, the experimentally derived amplification is 23.4 (averaged over two runs, 22.7 and 24.0). The experimentally derived amplification is smaller than the microwave amplifier gain due to transmission loss and the nature of the radiation coupling to the junction.
[28] Vibrational spectra of single MnCO molecules adsorbed on NiAl(110) surface have been obtained with STM-IETS. (Ref. 23). A low energy vibration at different energies is observed for each of the three types of MnCO that are imaged distinctly and can be converted from one type to another by applying a voltage pulse. This mode is assigned to the hindered rotation of CO. Here we show spectra for two of the three types of MnCO measured with the same tip.
[29] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998).