

# Theory of Elastic and Inelastic Tunnelling Microscopy and Spectroscopy: CO on Cu revisited

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Based on density functional calculations of an ordered CO structure and a CO dimer on Cu(111), we show that the Tersoff-Hamann approach to tunnelling in an STM junction and its generalization to vibrational inelastic tunnelling give a useful description of observed STM images and vibrational spectra and microscopy. In particular, this approach provides new physical understanding of vibrational inelastic tunnelling that should not only be useful for the development of single molecule vibrational spectroscopy and microscopy but also of single bond making and breaking by inelastic electron tunnelling in an STM junction.

**Keywords:** Place keywords here

## 1. Introduction

The spectacular advances in analyzing and synthesizing matter on the sub-10 nanometer scale have been made possible by the unique capabilities of the scanning tunnelling microscope (STM) of imaging (Binnig et al. 1982), characterization (Stipe 1998b), and manipulation of single atoms and molecules on surfaces (Eigler & Schweizer 1990). A key ingredient behind these capabilities is the highly localized tunnelling of electrons in space between the tip and the sample. Elastic electron tunnelling provides the basic mechanism for imaging whereas inelastic electron tunnelling (IET) from adsorbate vibrations provides the basic mechanism for chemical characterization of single molecules by vibrational spectroscopy and microscopy (Stipe 1998b), single molecule chemistry (Ho 2002), and controlled molecular and atomic manipulation. Vibrational spectroscopy based on IET was first realized in oxide junctions but involved a macroscopic ensemble of molecules with no spatial resolution (Lamb & Jaklevic 1966). Examples of molecular motions and chemistry induced by IET include atom and molecule transfer (Eigler 1991; Komeda et al. 2002), rotation (Stipe 1998a), desorption (Bartels et al. 1998, 1999), single bond breaking (Stipe et al. 1997) and making (Lee & Ho 1999; Hla et al. 2000), and mode-selective chemistry (Pascual et al. 2003). To fully exploit the capabilities of IET, one needs to develop physical concepts and understanding from theory and modelling.

Simple models of IET in vibrational spectroscopy and in single bond breaking have to a large extent been based on a single resonance level Hamiltonian including a coupling to a local oscillator – the local polaron (LP) model that has appeared in many different contexts in condensed matter and chemical physics (Gadzuk 1991).

The LP model has been used to estimate the vibrational intensity and to discuss the vibrational line shape in IET spectroscopy (Persson & Baratoff 1987; Mii et al 2002). This model was adapted to bond breaking using a truncated oscillator model for the reaction coordinate (Gao et al. 1992, 1997; Salam et al. 1994; Teillet-Billy et al. 2000). These studies identified two different regimes for bond breaking rates with characteristic current and bias dependencies. In the high tunnelling current limit where the tunnelling rate is more rapid than the vibrational relaxation rate, IET results in a quasi-Boltzmann distribution of the excited vibrational states corresponding to vibrational heating and the bond is broken by a large number of IET events. In the low tunnelling current limit, on the other hand, the bond is broken by a minimal number of IET events because an excited vibrational states has nearly time to equilibrate between the tunnelling events. The vibrational heating regime was also identified in a less specific model for the electron-vibration coupling (Walkup et al. 1993). The observed power-law dependencies of the transfer rate in Eigler's (1991) Atomic Switch and of the dissociation (Stipe 1997) and rotation rates (Stipe 1998a) of an oxygen molecule on a platinum surface were successfully explained by this model. The power-law dependence of bond breaking rates on the tunnelling current is very sensitive to the bias, which was exploited in the realization of the mode-selective chemistry by IET in an STM junction (Pascual et al. 2003).

As illustrated above these simple models have been important for the conceptual development of IET but have important limitations in the quantitative modelling of vibrational excitations by IET, because of their parameterized, restricted form of the electron-vibration coupling and lack of lateral spatial resolution of IET. Some of these limitations were addressed by Mingo & Makoshi (1999, 2000) in a simple semi-empirical, tight-binding model for the vibrational excitation probability of a chemisorbed molecule by IET.

The theory of elastic tunnelling in an STM junction by Tersoff& Hamann (1983, 1985) has played a very important role in providing simple physical concepts for the interpretation of STM images in terms of the local density of electron states at the position of the tip apex. Thus a generalization of this theory to IET is highly desirable and was accomplished by Lorente& Persson (2000b). Combined with density functional calculations, this theory was successful in explaining the IET data for vibrations in acetylene molecules on copper and provided new physical understanding such as the importance of cancellation of inelastic and elastic contributions to the tunnelling current and the role of the symmetries of the vibrational mode and molecular states in determining the lateral spatial dependence of the IET images, that is, vibrational microscopy. In a preliminary density functional study, this theory was also applied to some modes of the carbon monoxide molecule on a copper surface (Lorente& Persson 2000a). Since the recent molecule cascade experiments by Heinrich et al. (2002) involved in part detailed IET measurements of a similar system, we have revisited this problem and made a density functional study of the IET intensities and images from all vibrational modes of carbon monoxide in the  $\sqrt{3} \times \sqrt{3}R30^\circ$  structure on the (111) surface of copper. In addition, we have confirmed their observation of CO dimers on this surface from density functional calculations of STM images.

## 2. Theory

### (a) Tunnelling and local density of states

A detailed theoretical treatment of the electron tunnelling between an STM tip and adsorbed molecules on a metal surface is a daunting task. In particular, the unknown structure of the tip is a major problem. A physical transparent and tractable method that circumvents this problem by making a minimal number of assumptions about the structure of the tip was developed by Tersoff & Hamann (1983, 1985). The practical drawback of this method is the fact that the absolute conductance cannot be calculated so one is never sure that the right constant-current contours are sampled (Hofer 2003). This method is based on the Bardeen (1961) approximation for tunnelling and an  $s$ -wave approximation for the emitted electrons from the tip. At zero temperature and small tip-sample bias  $V$ , the differential conductance,  $\sigma(V)$ , is then found to be simply related to the local density of states (LDOS) of the isolated sample at the position,  $\vec{r}_0$ , of the tip-apex as,

$$\begin{aligned}\sigma(V) &\propto \rho(\vec{r}_0, \epsilon_F + eV) \\ &= \sum_{\alpha} |\psi_{\alpha}(\vec{r}_0)|^2 \delta(\epsilon_F + eV - \epsilon_{\alpha})\end{aligned}\quad (2.1)$$

Here  $\epsilon_F$  is the Fermi energy of the sample. In principle, the LDOS is an excited state property and gives the DOS for adding an electron or an hole to the system. As shown in the last step, the LDOS have a simple form in an one-electron approximation for these excited states in terms of one-electron wave functions  $\psi_{\alpha}(\vec{r})$  and energies  $\epsilon_{\alpha}$ .

### (b) Vibrational inelastic tunnelling

The basic principle of IET behind vibrational spectroscopy is deceptively simple. A tunnelling electron is allowed by the Pauli principle to excite an adsorbate vibrational mode as soon its energy with respect to the Fermi level of the sample is larger than the vibrational energy  $\hbar\Omega$ . The opening of this inelastic channel at a bias  $V = \hbar\Omega/e$  is then expected to result in an increase of the tunnelling current  $I$  corresponding to a discontinuity in  $\sigma$  and peak in the second order differential conductance  $\frac{d\sigma}{dV}$ . However, the opening of an inelastic channel affects in general also the elastic channel so that the change in the total tunnelling current does not necessarily need to be positive and the vibrational line shape  $L(V)$ , defined as  $\frac{d\sigma}{dV}(V)$  normalized to a background differential conductance  $\sigma_{bg}$ , is not necessarily symmetric.

A proper treatment of the non-adiabatic effects of the adsorbate vibration on the tunnelling conductance is obtained from a generalization of the LDOS in Eq. (2.1) to a many electron system interacting with a vibrational mode. At zero temperature one finds (Lorente & Persson 2000a,b),

$$L_0(V) = \frac{\frac{\partial \Delta\rho}{\partial V}(\vec{r}_0; \epsilon_F + eV)}{\rho_{bg}} \quad (2.2)$$

where  $\Delta\rho$  is the vibration-induced  $\rho$  and  $\rho_{bg}$  is the LDOS corresponding to  $\sigma_{bg}$ . There are two basic assumptions behind this result. First, the electron-vibration

coupling should be limited in space to the sample. Second, the vibrational relaxation rate should be much more rapid than the tunnelling rate so that the sample is close to equilibrium. The first assumption implies that any coupling through a long-range, dipole-like coupling is not handled properly. The second assumption can be relaxed by taking into account the non-equilibrium distribution over the vibrational levels sustained by IET current. To leading order in the electron-vibration coupling, one finds the following line shape,  $L_0(V)$ , for the excitation of the mode at positive  $V$  and zero temperature,

$$L_0(V) = \frac{\eta(\vec{r}_0; \Omega)(\gamma/2e) + \chi(\vec{r}_0; \Omega)(V - \hbar\Omega/e)}{\pi((V - \hbar\Omega/e)^2 + (\gamma/2e)^2)}, \quad (2.3)$$

Here  $\eta(\vec{r}_0; \Omega)$  is the integrated total strength of the line shape, that is, the relative change in  $\sigma$  across  $\hbar\Omega$ .  $\eta(\vec{r}_0; \Omega)$  has a positive contribution  $\eta_{inel}(\vec{r}_0; \Omega)$  that gives the probability for an electron with energy  $\hbar\Omega$  to excite the mode. The negative contribution  $\eta_{el}(\vec{r}_0; \Omega)$  to  $\eta(\vec{r}_0; \Omega)$  and the asymmetry parameter  $\chi(\vec{r}_0; \Omega)$  derive from the interference between an electron tunnelling directly or virtually exciting the mode while obeying the Pauli principle in the intermediate state. The width of  $L_0(V)$  is set by the vibrational damping rate  $\gamma$ . Note that at negative  $V$ ,  $L_0(V) = -L_0(-V)$  and  $\Omega \rightarrow -\Omega$ .

In an one-electron approximation such as provided by density functional theory, the line shape parameters in Eq. (2.3) turn out to have a relatively simple form. Typically, the density of one-electron states is slowly varying on the scale of  $\hbar\Omega$ , so that the quasi-static limit  $\Omega \rightarrow 0$  for the line shape parameters are justified. Moreover, these parameters can be expressed in a form that do not contain explicitly the electron-vibration coupling potential  $\delta v(\vec{x}) = \partial v / \partial q(\vec{x})$  where  $v(\vec{x})$  is the one-electron potential and  $q$  the vibrational coordinate. The basic quantity in these expressions is simply the first-order deformation  $\delta\psi_\alpha(\vec{r}_0)$  of an one-electron wave function  $\psi_\alpha(\vec{r}_0)$  at the Fermi level induced by a quasi-static displacement of the vibration with amplitude  $\delta q = \sqrt{\hbar/(2M\Omega)}$  where  $M$  is the mass associated with  $q$ . The line shape parameters are then given in terms of these wave function deformations at the tip apex by,

$$\eta_{inel}(\vec{r}_0) = \sum_{\alpha} |\langle \delta\psi_{\alpha} | \vec{r} \rangle|^2 \delta(\epsilon_{\alpha} - \epsilon_F) / \rho_{bg} \quad (2.4)$$

$$\eta_{el}(\vec{r}_0) = -2 \sum_{\alpha} |\text{Im}(\langle \delta\psi_{\alpha} | \vec{r} \rangle)|^2 \delta(\epsilon_{\alpha} - \epsilon_F) / \rho_{bg} \quad (2.5)$$

$$\chi(\vec{r}_0) = -2 \sum_{\alpha} \text{Re}(\langle \vec{r} | \delta\psi_{\alpha} \rangle) \text{Im}(\langle \delta\psi_{\alpha} | \vec{r} \rangle) \delta(\epsilon_{\alpha} - \epsilon_F) / \rho_{bg} . \quad (2.6)$$

In particular,  $\eta_{inel}$  has a simple physical form, which involves directly the vibration-induced deformations of the wave functions in the region of the tip-apex.

The remaining line shape parameter, the vibrational damping rate  $\gamma$  in Eq. (2.3), has in general contributions from both absorption and emission of electron-hole pairs or phonons (Langreth & Persson 1995). The electron-hole pair contribution  $\gamma_{eh}$  to  $\gamma$  is determined by the same electron-vibration coupling  $\delta v$  that determines the IET efficiencies in Eq. (2.3). In the same quasi-static limit, one arrives at the

following result for  $\gamma_{eh}$  (Hellsing & Persson 1984).

$$\gamma_{eh} = 4\pi\Omega \sum_{\alpha,\beta} |\langle \psi_\alpha | \delta v | \psi_\beta \rangle|^2 \delta(\epsilon_\alpha - \epsilon_F) \delta(\epsilon_\beta - \epsilon_F) \quad (2.7)$$

Note that the  $\Omega$  factor is introduced by the DOS for electron-hole pairs close to the Fermi level and cancels the  $\Omega$  dependence of the  $\delta q^2$  factor in  $\delta v$ .

Before closing this section, we need to comment on two other important well-known effects from IET spectroscopy in oxide junctions that will broaden the observed vibrational line shape (Lambe & Jaklevic 1968; Klein et al. 1973; Lauhon & Ho 2001). First, at non-zero temperatures the sharp Fermi distributions of the sample and tip will be smeared out and broaden  $L_0(V)$ . This broadening is given by convoluting  $L_0(V)$  twice by  $-\frac{df}{d\epsilon}(eV + \epsilon_F)$  where  $f(\epsilon)$  is the Fermi-Dirac distribution. Second,  $\frac{d\sigma}{dV}(V)$  is determined experimentally from the second harmonic of the tunnelling current when modulating the bias  $V$  with an amplitude  $\delta V$ . This modulation result in broadening of  $L_0(V)$  that is given by a convolution of  $L_0(V)$  with  $2J_2(V\delta V)/(V\delta V)^2$ . In a gaussian approximation for  $L_0(\omega)$ , the broadenings are about  $5.4k_B T$  and  $1.2\delta V$  from the temperature  $T$  and the modulation  $V$ , respectively.

### 3. Some details of the computational method

The bonding geometry, vibrational energies, and LDOS images of a chemisorbed CO molecule, and the line shape parameters have all been calculated from forces and one-electron states obtained from density functional calculations. These calculations were carried out using the projector augmented wave method as implemented in the VASP code (Kresse & Furthmüller 1996a,b). The exchange and correlation effects were represented by the generalized gradient approximation (GGA) (Perdew et al. 1992). The ordered  $(\sqrt{3} \times \sqrt{3})R30^\circ$  CO structure on the Cu(111) surface was represented by a single CO molecule on a 12 Cu layer slab in a super cell geometry, whereas the isolated CO dimer on the Cu(111) surface was represented by a CO dimer on a six layer slab with a  $(3 \times 3)$  unit cell. The thickness of the vacuum region of the super cells corresponded to 6 Cu layers. The kinetic energy cut-off for the plane wave basis set was set to 400 eV and the surface Brillouin zone were sampled by 81 and 9  $k$  points for the ordered CO structure and the CO dimer, respectively. The C and O atoms atom and the two outermost layers of Cu atoms were fully relaxed until the residual forces were less than 0.05eV/Å.

The energies of the vibrational modes at the  $\Gamma$  point of the surface Brillouin zone (SBZ) for the ordered CO structure on the rigid Cu surface were obtained from a diagonalization of the dynamical matrix. This matrix was generated from central differences of the forces on the C and O atoms as obtained by symmetric displacement of these atoms.

The technical aspects of calculations of the topographical images of the LDOS (Eq. 2.1), the inelastic efficiencies, (Eqs. 2.4, 2.5 and 2.6, and the vibrational damping rates (Eq. 2.7) using the Kohn-Sham states have been described in Ref. (Lorente & Persson 2000a). These calculations entail an analytical continuation of the tails of the wave functions to the tip-apex, a broadening of the discrete set of states in the super cell to a continuum and a calculation of matrix elements of the electron-vibration coupling via wave function overlaps for displaced configurations.

## 4. Results and Discussion

### (a) Chemisorption bond parameters

Density functional calculations give in general an excellent account of the geometric and vibrational structure of chemisorbed molecules on metal surfaces. A somewhat disturbing example has been the failure of the determination of the adsorption site of the CO molecule on metal surfaces. Typically, when using a semi-local approximation, such as GGA, for the exchange-correlation potential an hollow adsorption site is found to have the lowest energy for many surfaces in disagreement with experiments (Feibelman et al. 2001). Recently, Kresse et al. (2003) suggested a modification of this functional that might cure this problem. Here we have used the experimentally determined on-top adsorption site for the CO molecule with the C atom bonded to the Cu atom and the molecular axis perpendicular to the surface. The optimized interatomic bonding distances of the CO molecule are in within 0.01 Å of experiments. In the case of the CO dimer, the bond angle between the C-O bond and the Cu-C bond is very close to 180° but the molecular axes are found to be tilted away from the surface normal with about 7° in opposite directions. In the case of the ordered CO structure, the calculated energies for the two-fold degenerate, frustrated translation (FT) and rotation (FR), and the molecular (M) and internal stretch (I) are in good agreement with experimental data as shown in Table 1.

### (b) Topographical STM images

The observed STM images recorded at a constant current by Heinrich et al. (2002) have been simulated by topographical LDOS images. In Fig. 1, we show calculated images of the ordered CO structure and the CO dimer for a tip-apex – bare surface distance of about 9 Å. Note that the O atom is located about 3 Å from the surface so that tip-apex – O-atom distance is only about 6 Å. In the ordered structure, a CO molecule gives rise to a small depression with a corrugation of about 0.05 Å. This depression is an effect of the adsorbate-induced DOS being of predominantly  $2\pi^*$  character at  $\epsilon_F$ . The surface corrugation is found to be dramatically enhanced for the CO dimer, and a pronounced protrusion of about 0.5 Å develops between the two molecules and two depressions of about 0.3 Å on the opposite sides of the molecules. This result suggests that a bonding combination is formed between the  $2\pi^*$  molecular resonance states of the two molecules with a large weight at the Fermi level.

The calculated topographical images are in agreement with the observed images. Well-separated CO molecules on metal surfaces are in general imaged as depressions. In particular, isolated CO molecules and CO molecules in the  $\sqrt{3} \times \sqrt{3}R30^\circ$  structure on Cu(111) are imaged as depressions. However, the calculations underestimate the observed magnitude of about 0.5 Å for the depression. Note that in our earlier calculations of STM images of CO on the (111) and (100) surfaces of Cu, we did not find any depression because we considered a too short tip-apex–surface distance. For instance, the depression changes into a protrusion with a corrugation about 0.20 Å when the tip-apex – bare surface distance is shortened to about 6 Å. This uncertainty regarding the tip surface distance illustrates the drawback of the TH model that the observed tunneling conductance cannot be used to determine

the proper tip-surface distance. The STM image showing two depressions centered on the two neighboring lattice sites with a strong protrusion in between these two sites was attributed to a CO dimer and is well reproduced in the calculated image. No value for the corrugation of the STM image was quoted in the experiments but the image reveal that the corrugation is at least as large as the one observed for the isolated CO molecules in agreement with the calculated corrugation.

(c) *Vibrational inelastic tunnelling*

We have calculated the inelastic tunnelling efficiencies for all the four vibrational modes of the CO molecule in the ordered structure on Cu(111). In Fig. 2, we present contour plots of the calculated  $\eta(\vec{r})$  for these modes, which can be compared with observed vibrational microscopy images. Note that for this high coverage of CO molecules,  $\eta(\vec{r})$  from each molecule overlap in space so  $\eta(\vec{r})$  does not vanish at the surface-unit-cell boundary. The IET signals for the FT and the FR modes are found to be almost an order of magnitude larger than those for the I and the M modes. Moreover, an account of the two-fold degeneracies of the FT and FR modes increases this difference with a factor of two, as shown by the extremal values for  $\eta(\vec{r})$  listed together with the extremal values of  $\eta_{inel}$ ,  $\eta_{el}$  and  $\chi$  in Table 1. For all these modes we find that  $\eta_{inel}$  dominates  $\eta$  so in contrast to C<sub>2</sub>H<sub>2</sub> on Cu(100) there is no cancellation between inelastic and elastic contributions in this case. Finally, as indicated in Table 1,  $\eta$  is weakly dependent on the tip-surface distance so that the choice of a proper tip-surface distance is not critical.

The spatial shape of  $\eta(\vec{r})$  for a vibrational mode can be understood from the symmetries of the vibrational mode and the molecular states at the Fermi level as discussed for the C–H stretch modes of C<sub>2</sub>H<sub>2</sub> on Cu(100) in Lorente & Persson (2001). The sample states  $\alpha$  that contribute to the IET, Eq. (2.4), are those that have an overlap with molecular resonance states that give a dominant contribution to the DOS at the Fermi level such as the twofold degenerate  $2\pi^*$  resonance states for CO on Cu. These states have then the same symmetry character,  $E$ , as the FR and FT modes so that a deformation by these modes of these sample states will have a totally symmetric,  $A_1$  component and the resulting  $\eta_{inel}(\vec{r})$  has no nodal planes in agreement with the calculated one. In contrast, the I and M modes are totally symmetric and the corresponding deformations of the sample states that overlap with the  $2\pi^*$  states will not change their symmetry character and  $\eta_{inel}(\vec{r})$  will have a depression centered on the CO molecule. Furthermore, this character of these states is consistent with the lower IET intensities of these modes than for the FR and FT modes. States with  $E$  character have larger lateral kinetic energy in the vacuum region compared to  $A_1$  states and give a smaller contribution to the LDOS at the tip apex than  $A_1$  states.

Since both  $\eta_{inel}$  and  $\gamma_{eh}$  are determined by the same deformation of the electron-vibration potential, one would expect some correlation between these two parameters as discussed by Mingo et al. (2001). In Table 1, we have listed the calculated  $\gamma_{eh}$  for the four CO vibrational modes. These calculated values are, as indicated, in agreement with available experimental data for CO on a Cu(111) surfaces. The calculated  $\gamma_{eh}$  show no simple correlation with  $\eta_{inel}$  even if we correct for the electron-hole pair DOS factor,  $\hbar\Omega$ , present in  $\gamma_{eh}$ . For instance, this correction gives about the same values of  $\gamma_{eh}/\hbar\Omega$  for the FT and M modes but  $\eta_{inel}$  differ with more than

one order of magnitude. Note that if  $\gamma_{eh}$  would be the only contribution to  $\gamma$ , its small value of 0.008 meV would drive this mode far away from thermal equilibrium at typical values for IET currents in the range of 1-10 nA. However,  $\gamma$  is found to be dominated by one-phonon emission and absorption, resulting in a width of about 0.25 meV (Lewis & Rappe 1996) so that this mode is close to thermal equilibrium for these currents.

The calculated IET efficiencies and images are consistent with available experimental data for CO on Cu surfaces (Lauhon & Ho 1999; Heinrich et al. 2002; Moresco et al. 1999). The FR and FT modes are found to be the dominant ones in the IET, the M mode has never been observed and the I mode was found to be weak. The calculated IET image for the FR mode is in agreement with the observed IET image showing a maximum intensity at the center, falling off more or less symmetrically around the molecule. The relative changes of the discontinuities in  $\sigma$  for  $eV$  crossing  $\hbar\Omega$  are found to be as large 8% and 1.5 % for the FR and I modes of CO on Cu(001) (Lauhon & Ho 1999), respectively. This large value for the FR mode is consistent with the calculated value of about 16% and the value for the I mode was earlier shown to be accounted for by a long-range, dipole coupling (Lorente & Persson 2000a). No values for these discontinuities were quoted by Heinrich et al. (2002) but the displayed IET spectroscopy data indicated that the intensity of the FT mode is slightly less than the FR mode in accordance with the calculated  $\eta$ .

In Fig. 3, we show a simulated IET spectrum for the FR mode based on the calculated values for the line shape parameters and typical values for the tip and sample temperature and modulation voltage. Here only the electron-hole pair contribution to  $\gamma$  have been included and any phonon contribution from anharmonicity in the molecule-surface bond or any contribution from a dispersion of this mode is ignored. As shown in Fig. 3, the intrinsic broadening of the vibrational line shape is not resolved but the asymmetry survives the temperature and modulation broadening. The calculated broadening accounts to a large part for the observed broadening of the IET spectrum for the FR mode by Heinrich et al. (2002) but the positive and negative  $V$  regions of the spectrum do not simply suggest a definite asymmetry.

## 5. Concluding Remarks

In conclusion, we have illustrated from density functional calculations of an ordered CO structure and a CO dimer on Cu(111) that the Tersoff & Hamann approach to tunnelling in an STM junction and its generalization to vibrational inelastic tunnelling by Lorente & Persson give a useful description of STM images and vibrational spectra and microscopy of chemisorbed molecules on metal surfaces. In particular, this approach provides new physical understanding of vibrational inelastic tunnelling that should not only be useful for the development of single molecule vibrational spectroscopy and microscopy but also of single bond making and breaking by inelastic electron tunnelling in an STM junction. Developments that should be of key importance for the analysis and synthesis of matter on the sub-10 nanometer scale by the scanning tunnelling microscope.

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## References

- Bardeen, J. 1961 *Phys. Rev. Lett.* **6**, 57.
- Binnig, G., Rohrer, H., Gerber, Ch., & Weibel, E. 1982 *Phys. Rev. Lett.* **49**, 57.
- Bartels, L., Meyer, G., Rieder, K.-H., Velic, D., Knoesel, E., Hotzel, A., Wolf, M. & Ertl, G. 1998 *Phys. Rev. Lett.* **80**, 2004.
- Bartels, L., Wolf, M., Klamroth, T., Saalfrank, P., Kühne, A., Meyer, G. & Rieder, K.-H. 1999 *Chem. Phys. Lett.* **313**, 544.
- Eigler, D. M., & Schweizer, E. K. 1990 *Nature* **344**, 524.
- Eigler, D. M., Lutz, C. P. & Rudge, W. E. 1991 *Nature* **352**, 600.
- Feibelman, P., Hammer, B., Nørskov, J. K., Wagner, F., Scheffler, M., Stumpf, R., & Dumesic, J. 2001 *J. Phys. Chem. B* **105**, 4018.
- Gadzuk, J.W. 1991 *Phys. Rev. B* **44** 13466.
- Gao, S., Persson, M., & Lundqvist, B. I. 1992 *Solid State Comm.* **84**, 271.
- Gao, S., Persson, M., & Lundqvist, B. I. 1997 *Phys. Rev. B* **55**, 4825.
- Heinrich, A. J., Lutz, C. P., Gupta, J. A., & Eigler, D. M. 2002 *Science* **298**, 1381–1387.
- Helsing, B. & Persson, M. 1984 *Phys. Scr.* **29**, 360.
- Hirschmugl, C. J., Williams, G. P., Persson, B. N. J. & Volokitin, A. I. 1994 *Surf. Sci.* **317**, 1141.
- Hirschmugl, C. J., Williams, G. P., Chabal, Y. J. & Hoffmann, F. M. 1994 *J. Vac. Sci. Technol. A* **12**, 2229.
- Hla, S. W., Bartels, L., Meyer, G. & Rieder, K. H. 2000 *Phys. Rev. Lett.* **85**, 2777.
- Ho, W. 2002 *J. Chem. Phys.* **117**, 11033–11061.
- Hofer, W. A. 2003, *Prog. Surf. Sci.* **71** 147.
- Klein, J., Leger, A., Belin, M., Defourneau, D. & Sangster, M. J. L. 1973 *Phys. Rev. B* **7**, 2336.
- Komeda, T., Kim, Y., Kawai, M., Persson, B. N. J. & Ueba, H. 2002 *Science* **295**, 2055–2058.
- Kresse, G. & Furthmüller, J. 1996 *Comput. Mater. Sci.* **6**, 15.
- Kresse, G. & Furthmüller, J. 1996 *Phys. Rev. B* **54**, 11 169.
- Kresse, G., Gil A., & Sautet P. 2003 *Phys. Rev. B* **68**, 073401.
- Lambe, J. & Jaklevic, R. C. 1966 *Phys. Rev. Lett.* **17**, 1139.
- Lambe, J. & Jaklevic, R. C. 1968 *Phys. Rev.* **165**, 821.
- Langreth, D. C. & Persson M. 1995 Vibrational relaxation and dephasing of molecules adsorbed on metal surfaces. In *Laser Spectroscopy and Photochemistry on Metal Surfaces* (ed. H. L. Dai & W. Ho) Advanced series in Physical Chemistry, vol. 5, ch. 13, p. 498 World Scientific, River Edge, New Jersey.
- Lauhon, L. J. & Ho, W. 2001 *Rev. of Sci. Instr.* **72**, 216–223.
- Lauhon, L. J. & Ho, W. 1999 *Phys. Rev. B* **60**, R8525.
- Lee, H. J. & Ho, W. 1999 *Science* **286**, 1719–1722.
- Lorente, N. & Persson, M. 2000 *Faraday Discussions* **117**, 277.
- Lorente, N. & Persson, M. 2000 *Phys. Rev. Lett.* **85**, 2997.
- Lorente, N., Persson, M., Lauhon, L. J. & Ho W., 2001 *Phys. Rev. Lett.* **86**, 2954.
- Lewis, S. P. & Rappe, A. 1996 *Phys. Rev. Lett* **77** 5241.
- Mii, T., Tikhodeev, S. & Ueba, H. 2002 *Surf. Sci.*, **502/503**, 26–33.
- Mingo, N. & Makoshi, K. 1999 *Surf. Sci.* **438**, 261–270.

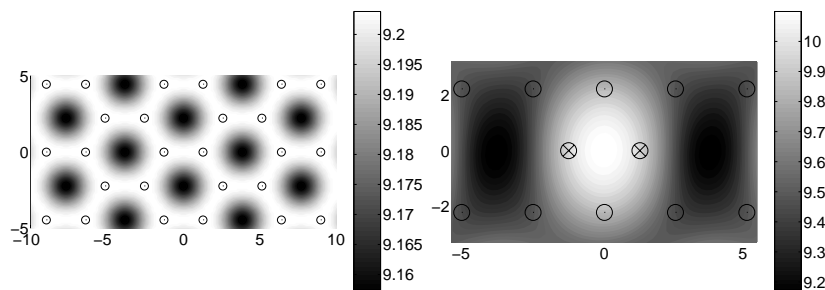


Figure 1. Calculated topographical images of the LDOS for (A)  $(\sqrt{3} \times \sqrt{3} R30^\circ)$ CO and (B) the CO dimer on Cu(111). The crosses and circles indicate the adsorption sites of the CO molecule and the positions of the Cu atoms in the outermost surface layer, respectively. The tip–apex–surface distance is with respect to the position of this layer.

- Mingo, N. & Makoshi, K. 2000 *Phys. Rev. Lett.* **84**, 3694.
- Mingo, N., Makoshi, K., Mii, T. & Ueba, H. 2001 *Surf. Sci.* **482-485** 261-270.
- Moresco, F., Meyer, G. & Rieder, K.-H. 1999 *Mod. Phys. Lett. B* **13**, 709.
- Pascual, J. I., Lorente, N., Song, Z., Conrad, F. & Rust, H.P. 2003 *Nature* **423**, 525.
- Perdew, J. P., Chevary, J. A., Vosko, S. H., Jackson, K. A., Pederson, M. R., Singh, D. J. & Fiolhais, C. 1992 *Phys. Rev. B* **46**, 6671.
- Persson, B.N.J. & Baratoff, A. 1987 *Phys. Rev. Lett* **59** 339.
- Salam, G. .P., Persson, M., & Palmer, R. E. 1994 *Phys. Rev. B* **49**, 10655.
- Stipe, B. C., Rezaei, M. A. & Ho, W. 1998 *Science* **279**, 1907.
- Stipe, B. C., Rezaei, M. A. & Ho, W. 1998 *Science* **280**, 1732.
- Stipe, B. C., Rezaei, M. A., Ho, W., Gao, S., Persson, M. & Lundqvist, B. I. 1997 *Phys. Rev. Lett.* **78**, 4410.
- Teillet-Billy, D., Gauyacq, J. P., & Persson, M. 2000 *Phys. Rev. B* **62**, R13306.
- Tersoff, J. & Hamann, D. R. 1983 *Phys. Rev. Lett.* **50**, 1998.
- Tersoff, J. & Hamann, D. R. 1985 *Phys. Rev. B* **31**, 805.
- Walkup, R. E., News, D. M. & Avouris, Ph. 1993 *Phys. Rev. B* **48**, 1858.

## 6. Figures

## 7. Tables

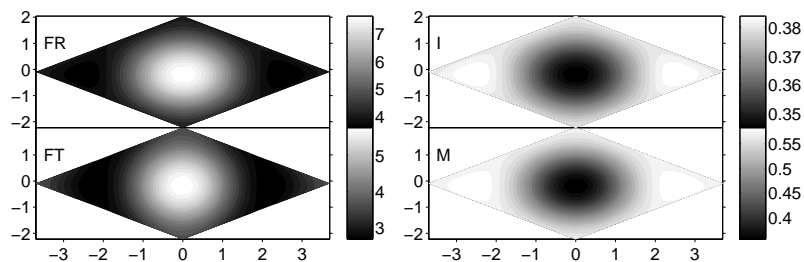


Figure 2. Calculated images of the total inelastic efficiencies,  $\eta(\vec{r})$ , for the frustrated translational (FT) and rotational (FR) modes, and the molecular (M) and internal (I) stretch of CO on Cu(111). The tip-apex-surface distance is 9 ( $\text{\AA}$ ).

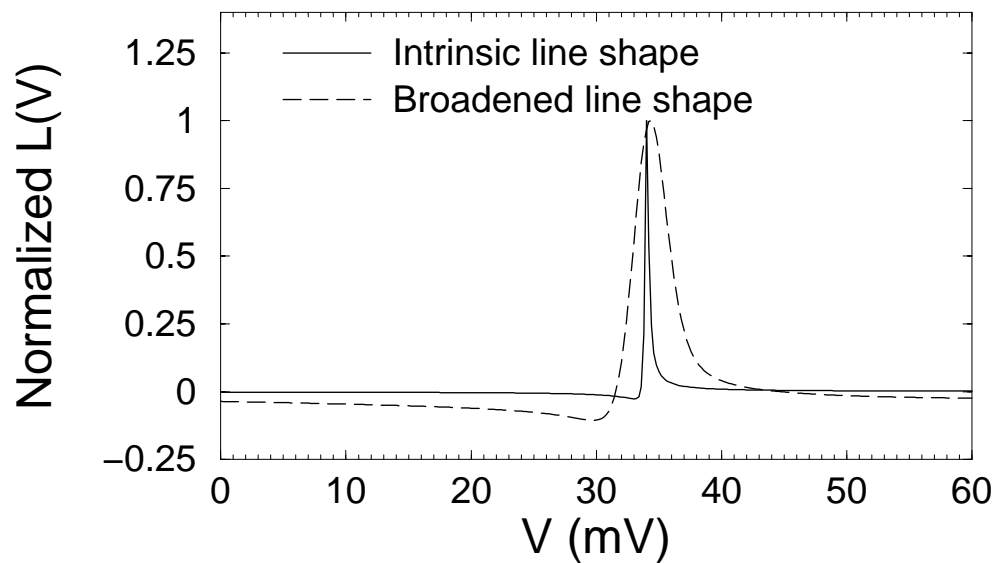


Figure 3. Simulated inelastic electron tunnelling spectrum for the frustrated rotational (FR) mode of  $(\sqrt{3} \times \sqrt{3}R30^\circ)$ CO on Cu(111). The solid line gives the intrinsic line shape function  $L(\omega)$ , whereas the dashed line includes a temperature and a modulation broadening corresponding to  $T = 5$  K and  $\delta V = 1.4$  mV, respectively. The line shape functions have been normalized to their maximum values

Table 1. *Calculated energies, line shape parameters, and electron-hole pair broadenings for the vibrational modes of CO on Cu(111).*

(Same tip-surface distance as in Fig. 2.  $\eta$  changes from 10% to 14.6% and 14.6 % to 18.2% when the tip-surface distance changes from 8 to 10 Å for the FR and FT modes, respectively, whereas the corresponding changes of the remaining modes are less than 0.1% units. The values within the parentheses are taken from experiments: <sup>(a)</sup>(Heinrich et al. 2002); <sup>(b)</sup>(Hirschmugl et al. 1994a); <sup>(c)</sup>(Hirschmugl et al. 1994b))

| mode | $\hbar\omega$ (meV)      | $\eta_{tot}$ (%) | $\eta_{inel}$ (%) | $\eta_{el}$ (%) | $\eta_{as}$ (%) | $\gamma_{eh}$ (meV)           |
|------|--------------------------|------------------|-------------------|-----------------|-----------------|-------------------------------|
| FT   | 3.7 (4) <sup>(a)</sup>   | 11.8             | 12.2              | -0.3            | -1.7            | 0.0078 ( 0.01) <sup>(c)</sup> |
| FR   | 34 (35) <sup>(a,b)</sup> | 15.6             | 16.8              | -0.9            | 5.2             | 0.31 ( 0.6) <sup>(c)</sup>    |
| M    | 42 (42) <sup>(b)</sup>   | 0.6              | 0.7               | -0.2            | -0.2            | 0.084                         |
| I    | 253 (258) <sup>(b)</sup> | 0.4              | 0.5               | -0.1            | 0.2             | 0.30                          |