Intensity studies of inelastic electron tunneling spectra

Glenn Agnolet\textsuperscript{a,\,*}, Darin T. Zimmerman\textsuperscript{b}

\textsuperscript{a}Department of Physics, Texas A\&M University, College Station, TX 77843-4242, USA
\textsuperscript{b}Department of Physics, Penn State Altoona College, Altoona, PA 16601-3760, USA

Abstract

Inelastic electron tunneling spectroscopy (IETS) using metal–insulator–metal (MIM) tunnel junctions is an established technique for studying the vibrational modes of molecules adsorbed on metal surfaces. We are examining a new geometry for IETS in which the oxide layer of the MIM junction is replaced by an atomically thin gas \textit{lm}. Clean junctions in which the barrier is composed of pure neon exhibit Ohmic behavior except in the region near zero bias. When the neon barrier is doped with acetylene molecules, we observe peaks corresponding to the vibrational modes of these molecules. An analysis of the inelastic peak intensities indicates that dipole scattering is not the principle mechanism of the electron–molecule interaction in this geometry.

PACS: 33.20.\textemdash t; 73.40.Gk; 73.40.Rw; 87.64.Je

Keywords: Inelastic electron tunneling spectroscopy; Molecular vibrational spectroscopy; Point contact spectroscopy

Recently, we demonstrated that self-assembling tunnel junctions (SATJs) \cite{1} have the necessary stability to perform inelastic electron tunneling spectroscopy (IETS) of molecules adsorbed on metal surfaces \cite{2}. The SATJ is formed by pressing together two long, fine metallic wires whose separation is set by an atomically thin gas barrier \textit{lm}. The molecules to be studied can either be deposited directly onto the metal surfaces or coadsorbed with the \textit{lm}. Using standard AC modulation techniques, we simultaneously measure the total current, $I$, the conductance, $\sigma = dI/dV$, and the derivative of the conductance, $d\sigma/dV$. Inelastic signals due to the excitation of molecular vibrational modes appear as peaks in $(d\sigma/dV)/\sigma$.

Junctions made with ultra-pure neon show no discernable inelastic features apart from a significant suppression of the conductance near zero bias \cite{3}. When a 1:3 gas mixture of C\textsubscript{2}H\textsubscript{2} and Ne is deposited onto Pt wires, we observe peaks corresponding to the vibrational modes of the C\textsubscript{2}H\textsubscript{2} molecules. The data are fit to a theoretical function that includes two components: (i) a background function that includes terms to model the zero bias feature and (ii) Lorentzian peaks convolved with the modulation function (thin solid curves). The intensity of an individual mode is proportional to the integrated area of the fitted peak or equivalently, the fractional change in the conductance, $\Delta\sigma/\sigma$, at the vibrational energy ($h\omega$).

From the energies of the peaks, we can distinguish between molecules that are chemisorbed on the Pt surface and those embedded in the neon matrix (Fig. 1). Five peaks in Fig. 1 (dashed lines) match the modes of chemisorbed C\textsubscript{2}H\textsubscript{2} on Pt(111) as observed by EELS \cite{4}. The remaining peaks (solid lines) match the known infrared and Raman-active gas-phase C\textsubscript{2}H\textsubscript{2} vibrational modes \cite{5} and therefore correspond to molecules that are incorporated within the Ne matrix.

To be consistent with a dipole-scattering mechanism \cite{6}, the IETS intensities should scale as the square of the dipole matrix elements as determined by infrared spectroscopy. Since the effective C\textsubscript{2}H\textsubscript{2} surface coverage is not known, we only examine intensity ratios, since the ratio, unlike the absolute intensity, should be insensitive to the coverage.

If the C\textsubscript{2}H\textsubscript{2} molecules within the neon matrix have random orientations, then the gas-phase IETS intensities should have the same ratio as the corresponding modes in the infrared. For the asymmetric C–H stretching and
bending modes (407 and 91 meV) this ratio is 12 [7]. If, however, the C$_2$H$_2$ molecules are preferentially aligned with their C–C axes parallel to the metal surface, then due to screening of the dipole moments by image dipoles in the metal, one expects an even larger ratio. The equivalent IETS ratio for the data in Fig. 1, $(\Delta \sigma/\sigma)_{91}/(\Delta \sigma/\sigma)_{407}$, is only 2.9.

Since measured values of the dipole moments of chemisorbed C$_2$H$_2$ on Pt are not available, we compare our data with recent theoretical work [8]. Depending on the orientation of the molecule on the Pt surface, the theoretical intensity ratio for the symmetric C–H stretching and bending modes (368 and 123 meV) ranges from 1 to 5. Experimentally, we obtain $(\Delta \sigma/\sigma)_{123}/(\Delta \sigma/\sigma)_{368} = 0.12$.

The large disparity between the experimental IETS ratios and those predicted from theory strongly suggests that the electron–molecule interaction in this tunneling geometry cannot be modeled by a simple dipole interaction [6] and that other mechanisms must be included to properly describe the interaction [9–11].

**Acknowledgements**

This work was supported by the National Science Foundation, the Texas Advanced Research Program, and the Robert A. Welch Foundation.

**References**