INTRODUCTION

Shapes of molecules are ultimately determined by how one molecule sees another. This forms the working principle of the highest resolution scanning probe microscopes, which rely on a small test molecule attached to the probe to image another through the sensed intermolecular forces (1–5). The concept is most closely realized in atomic force microscopy using cantilevers terminated with a single carbon monoxide molecule (CO-AFM) (2), where interaction potentials due to electrostatic, dispersive, and Pauli repulsion forces acting on successively shorter range are sampled as a function of approach between CO and targeted molecules. At closest approach, the repulsive wall of interaction potentials images the ball-and-stick structure of molecules (6), with resolution sufficient to make structural assignments of unknown molecules (7). At a longer range, electrostatic forces are interrogated, and CO-AFM operating in the Kelvin probe force mode (8) has been used to image intramolecular charge distributions (9). Forces localized on one molecule are contrasted with a mechanical cantilever, although the measurement entails the sum over all interactions between tip and substrate. A stiff cantilever, with high-quality factor and 0.2 Å oscillation amplitude, is used to localize the sampled forces (10). With the demonstration that the vibrations of a single tip-attached CO can be detected through tip-enhanced Raman scattering (TERS), we suggested TERS-related molecular force microscopy (TERS-mfm) as a direct application of single-molecule vibrational spectroscopy (11). Here, we present the realization of the concept. Dispensing entirely with cantilevers, we use the molecular spring of CO attached to the tip apex of a scanning tunneling microscope (STM) as a force sensor and transducer. We implement TERS-mfm in the range where electrostatics dominate the intermolecular forces. In addition, by taking advantage of the vibrational Stark effect on the CO stretch (12), we interrogate electrostatic fields within single metalloporphyrin molecules adsorbed on Au(111). Molecule-metal charge transfer, structure-specific intramolecular polarization, counter polarization of surface electrons, and atomically resolved hydrogen bonds are among the unique observables that are imaged and quantified.

TERS-mfm may be recognized as the single-molecule limit of microelectromechanical sensors (MEMS). Among the notable operating specifications in this limit are extreme localization of the sensor to the 1.1 Å bond length of CO, amplitude of motion limited to single quantum excitation $\Delta r = |\langle 1|r|0\rangle| = 0.034$ Å, high stiffness $k = 1.7 \times 10^7$ N/m, and optical operating frequency $v = 10^{14}$ Hz, whereby the measurements are transferred to the spectral domain, with practically instantaneous response and multiplexing advantage. The already demonstrated resolvable frequency shift of the molecular oscillator, $\Delta v \sim 0.1$ cm$^{-1}$, establishes the detectable force $F = 2k\Delta r\Delta v/v \sim 0.5$ pN (11), which competes favorably with the advanced quartz cantilevers used in CO-AFM (10). The key development that enables TERS-mfm is the ~12 orders of magnitude signal enhancement necessary to raise the feeble Raman signal from a single CO molecule to levels useful for force microscopy. Detection of Raman scattering on single CO molecules was demonstrated previously at the plasmonic junction of fusing silver nanospheres, with large enhancement ascribed to tunneling charge transfer plasmons (13). A formal treatment of the scattering process in this regime (14) and explicit time-dependent density functional simulations of the photofield-driven tunneling current at the CO-STM junction (15) provide the background for the present development.

Despite the simplicity of a diatomic molecule, the electronic structure of CO is unusual. The free molecule carries 0.12-D dipole, with negative pole on carbon and negative charge density dangling from both oxygen and carbon ends (16). The sign of its apparent dipole upon adsorption on metals has led to ambiguity, necessitating explicit electronic structure calculations to interpret images obtained with CO-terminated tips (17). As the diatomic with the largest bond energy, the C–O stretch is stiff. Therefore, mechanical stresses are principally transmitted to the soft, frustrated rotation and translation modes (4, 18). However, because of its combined electric and mechanical anharmonicity, the CO stretch has a large Stark tuning rate (STR), $\partial E/\partial r$ (12), which makes it an effective molecular transducer of electrostatic fields $E = -\partial V_{es}/\partial r$ generated by local charge distributions

$$V_{es}(r) = \int \frac{p(r')}{|r-r'|} dr'$$  \hspace{1cm} (1)

In this context CO has been used to probe electrostatic potentials at surfaces and interfaces (19) and plasmonic junctions (20, 21) in proteins and enzymes (22). We use it here as a scanning electrometer. Because of its weak binding to silver, CO preferentially attaches to the apex of silver tips. The same consideration limits the measurements to long-range intermolecular interactions governed by electrostatics. As we show, the vibrational frequency shift maps out the $E$-field along
the tip axis, while the pendular motion manifested through the line-
width probes lateral electrostatic forces. Since the bond order, bond
energy, and therefore STR of CO depend on binding site and geome-
try, it is useful to calibrate the molecular electrometer before its use.
The measurements are carried out in an ultrahigh vacuum (UHV)
STM operating at 6 K (see Materials and Methods).

RESULTS
Calibration of the molecular electrometer
The inset of Fig. 1 shows the TERS spectrum of $^{12}$C$^{18}$O attached to the
silver tip apex. It consists of a single line, with center frequency that
shifts upon varying the junction bias. Figure 1 illustrates this for
tunneling gap fixed at $g = 5.5$ Å. The curve fits the quadratic form

$$\bar{v}(V_b; g) = \bar{v}(0; g) - aV_b - \frac{1}{2} bV^2_b$$

with linear and quadratic coefficients, $a = 19.3$ cm$^{-1}$/V and $b =
0.73$ cm$^{-1}$/V$^2$. To obtain absolute values, it is necessary to relate
the spectral shift to the local field, and the necessary information
is extracted from the gap dependence of the frequency shown in
Fig. 1 (A and C). The data can be fit to

$$\bar{v}(V_b; g) = \bar{v}_{g \rightarrow \infty} - c \frac{V_b - \Delta \phi}{g + d}$$

where $g + d$ defines the effective length over which the applied bias
drops, and $\Delta \phi = \phi_{Au} - \phi_{Ag}$ is the contact potential between the gold
substrate and silver tip. The latter is directly determined by the
crossing point between the asymptotic limit $\bar{v}_{g \rightarrow \infty}$ of the gap
dependence and the bias dependence (see Fig. 1A). The extracted
value $\Delta \phi = 0.78$ V is larger than the difference in work functions of
Au(111) and Ag(111) of 0.57 V (23), which is rationalized by the
positive charge on protruding Ag atoms (24). The obtained value of
d = 2.8 Å is a good fraction of what may be estimated ($d_0 \sim 3.5$ Å) as
the physical distance between the O atom terminus and the image
plane on the silver tip (25). Along the voltage drop between the gold
and silver electrodes, CO acts as a capacitor, with relative dielectric
constant $\varepsilon_r = d_0/d - 1.2$ (see fig. S2), as expected when molecular
orbitals are not aligned with the Fermi level (26). Converting the
applied bias to local field $E_l = V_b/(g + d)$ generates the calibration
curve of the molecular field meter, which is cast in more transparent
notation

$$\bar{v}(E_l) = \bar{v}(0) - \Delta \mu E_l - \frac{\Delta \alpha}{2} E_l^2$$

The magnitude of the linear coefficient is $\Delta \mu = \langle 1|\mu|0 \rangle = a(g + d) =
160$ cm$^{-1}$ V$^{-1}$ Å$^{-1}$ (0.095 D) is in excellent agreement with the pre-
diction of the density functional theory (DFT) calculations for CO
adsorbed on tipped silver (15). The sign of effective dipole fluxes upon
adsorption (15), and the linear STR is nearly three times that of
the free molecule (see fig. S3). While contact potentials change upon
reshaping the tip apex and quadratic coefficients vary on different tips,
the linear Stark coefficients show little tip-to-tip variation (see fig. S4).
It may be useful to note that the frequency shift, $\Delta \nu = \bar{v}(E) - \bar{v}(0)$, is a
direct measure of mechanical force, $F_m$, with a conversion factor of
5.8 pN cm$^{-2}$ given by the vibrational constants of CO.

TERS intensity as optical field meter
The line intensity determined by the TERS mechanism gives an addi-
tional imaging principle. We can extract the Raman scattering cross sec-
tion of the tip-adsorbed CO from the quadratic Stark tuning coefficient
in Eq. 4, $\Delta \alpha = \langle 1|\alpha|0 \rangle = -50$ cm$^{-1}$ V$^{-2}$ Å$^{-2}$ ($8.8 \times 10^{-30}$ cm$^3$)

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^2}{\lambda_0^4} |\langle 1|\alpha|0 \rangle|^2 = 4.8 \times 10^{-31}$ cm$^3$/sr

\[ Eq. 5 \]

Fig. 1. Calibration of the molecular electrometer. (A) Bias dependence with a gap fixed at 5.5 Å (set at 0.1 nA, +1.2 V). The inset shows the CO line spectrum. (B) Gap
dependence of Raman intensity and (C) C-O stretching frequency. All data are recorded with an excitation at $\lambda = 634$ nm and an incident intensity of $\sim 5 \mu W/\mu m^2$. 

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where $\lambda_i$ and $\lambda_s$ are the wavelengths of incident and scattered photons. The measured value is 50\% larger than that of the free molecule. Under the experimental conditions ($I = 5 \mu W/\mu m^2$, $\Delta \Omega = 2.7 \pi s$), we would expect a scattering rate of $I_0 = 5 \times 10^{-10} \ s^{-1}$ from one molecule. The observed count rates of $5 \times 10^7 \ s^{-1}$ imply enhancement by a factor of 10\%.

These large factors are associated with the combined effects of electromagnetic and chemical (CM) enhancement mechanisms (27), associated with the displacement field $D = E + 4\pi p$ confined between tip plasmon and its image in the metal substrate. The displacement current, $dD/dt$, is common to the series capacitors consisting of the vibrating CO, vacuum gap, and targeted molecule. In the hardwired CO, the CM arises from the charge transfer photocurrent through the projected density of states (DOS) of the targeted molecule. In the hardwired CO, the CM arises from the charge transfer photocurrent through the projected density of states (DOS) of the targeted molecule.

**Peering inside molecules**

To illustrate the method, we consider two members of the porphyrin family: cobalt(II)-tetraphenylporphyrin (CoTPP) and zinc(II)-etioporphyrin (ZnEtio), evaporated on an atomically flat Au(111) substrate. Given their ubiquity in nature and importance of their applications in catalysis and molecular optoelectronics, researchers extensively investigated metalloporphyrins on metal surfaces (30–32). It is known that CoTPP saddles upon adsorption on coinage metals (33, 34), while ZnEtio remains fairly flat (35). TERS-mfm reveals very different intramolecular charge distributions for these seemingly similar molecules. Figure 2 summarizes the measurements and simulations carried out on ZnEtio. The data consist of simultaneously recorded STM- and TERS-relayed images extracted from TERS spectra recorded on every 0.5 \ Å × 0.5 \ Å pixel with an acquisition time of 1 s/pixel. We then filter the intensity and linewidth maps for clarity. The STM intensity and linewidth maps are color-coded using the Stark shift on the STM CH topography. The common image size is 23 \ Å × 23 \ Å. The set point is 0.1 nA, 1.2 V.

The STM topography does not contain direct information about charges. The do...
a depression at the center instead of the maximum seen in the experi-
ment (see fig. S10). The general agreement validates the assumptions
that the Stark effect dominates the $\Delta\nu$ map, CO is vertically aligned
at this bias (1.2 V), and in the range of measurements, electrostatics
dominates the intermolecular forces between CO and ZnEtio. However,
the computed charge distribution appears to be more strongly local-
ized on the periphery than in the experiment. Whether in theory or ex-
periment, forces are the observables. Their inversion to extract charge
distributions is generally not unique. With that in mind, we provide
in Fig. 2 the Löwdin projection and the charge deformation obtained
as the density difference between the free and adsorbed molecule. The
former localizes charges on atoms, with positive charge mostly carried
by the hydrogens. The latter shows delocalized charge with radially
polarized periphery. The experiment suggests that the aromatic HOMO
carries the charge. The latter is consistent with a previous analysis of
the ZnEtio$^{-}$ radical anion prepared on a thin oxide, where it has been shown
that, because of the high symmetry of the planar molecule, the dynamic
Jahn-Teller effect imposes a ring current (35). This vibronic effect is
absent in the DFT calculations.

The linewidth of CO serves as a sensitive probe of lateral electrostatic
fields. The observed width on the macrocycle ring is near the instrument
limit (FWHM = 4.5 cm$^{-1}$). It broadens on the central atom and nearly
doubles in width on a ring outside the molecule. The observed break
in the outer ring is due to interference from another nearby ZnEtio.
Consistent with the conservative nature of electrostatic forces, the lack
of correlation between width and intensity maps establishes that the
broadening is not due to dissipation. The close correspondence between
the linewidth map and the computed in-plane electrostatic field, $|E_x + E_y|$, which reaches $\sim 10$ meV/Å on a ring outside the molecule, establishes
that the spatial variation in linewidth arises from lateral forces. We
can associate the spectral width with the angular distribution of CO
sampled by the pendular (frustrated translation) motion, which, at
2 meV (4), is the only accessible state at 6 K. We subject the pendular
motion of a dipole in an electrostatic field to torque that we can sense
through its modified angular frequency $\nu = \sqrt{\kappa + \mu E}/I$. When the
field is aligned with the dipole, the motion stiffens, and its angular
distribution narrows; therefore, the spectral width of the stretch
sharpens. This explains the observed line narrowing on the positively
charged ring, where the requirement of a vertical field $E \sim \kappa/\mu$ can be
satisfied if we assume the dipole to arise from the dangling 0.2e$^{-}$
charge on oxygen (for $\mu = 3.5$ D and $\kappa/\mu = 0.24$ V/Å; see fig. S5).
Upon falling off the molecule, the mode softens, and its thermal occu-
pation increases; therefore, the line broadens. While this explains
the principle of imaging contrast through linewidths, larger area
scans clarify that, both here and in the case of CoTPP, Friedel oscilla-
tions of surface electrons, known to be induced by charged adsorbates
(37), are being imaged (see below).

Figure 3 shows the equivalent set of images for a CoTPP molecule. In
the STM topography, the $C_4v$ symmetry of the free molecule is reduced
to $C_2$ because of the saddling distortion, which can be more clearly seen
in the TERS relayed images. The CC intensity map shows the inequiv-
alent dim (up) and bright (down) pyrroles. The polarization associated
with the distortion is relayed in the CC $\Delta\nu$ map, where a potential drop
of $\sim 1$ V is seen to extend along the edges of the lower pyrroles. The
CC $\Delta\nu$ image is reproduced by the computed $E_y$ field calculated at a
height of 4 Å above the molecular plane, and the linewidth images are
adequately reproduced by the computed lateral field, $|E_x + E_y|$. The
agreement between experiment and theory validates the scanning mol-
ecular electrometer and gives confidence to the dissection of previously
unknown charge distributions in what may be considered a weakly
bound molecule on gold.

Contrary to previous x-ray photoelectron spectroscopy analysis,
which assigns the charge transfer from gold to Co (38), and consistent
with a previous DFT analysis (34), we find that nearly a unit charge is
transferred from CoTPP to Au. This is extracted from the present DFT
calculations and separately established by modeling the Stark shift maps
and approach curves recorded on Co and pyrroles using a charged rect-
angular plate decorated with two line charges (fig. S6). The charge trans-
fer is from the macrocycle, rather than Co. We corroborated this by
observing the Kondo resonance of Co(II), which establishes that cobalt
retains its unpaired $d_{3d}$ electron configuration (see fig. S7). Once again,
the Löwdin projection localizes the positive charge on the peripheral
hydrogens, and we directly verified this by the experiment in this case.
We show in Fig. 3A that the contours of the largest spectral shift in the
CH $\Delta\nu$ image, at a potential of 1 V ($\Delta\nu = -20$ cm$^{-1}$) relative to gold,
are sharply localized on two pairs of atoms separated by 2.5 and 4.6 Å,
respectively. The former aligns with the hydrogens of the lower pyrrole,
while the latter aligns with the nearby hydrogen atoms on the phenyl
groups (circled in red in Fig. 3A). The four atomically resolved distribu-
tions highlight the spatial resolving power of the method, when such
features exist. Here, they suggest hydrogen bonding between CO and
the positively charged H atoms governed by electrostatic bonding be-
tween the dangling electron charge on oxygen and acidic hydrogens.
The same bonding motif was recently reported in CO-AFM measure-
ments (39). As we stepped up the potential to 0.8 V relative to gold, the
distributions merge and appear as the line charge of acidic hydrogens on
the lower pyrroles (Fig. 3A), followed by the trace of the H atoms dec-
orting the pocket between the pyrroles and phenyl rings. In effect, the
hydrogens are polarized through induction due to the charge transferred
from the physisorbed molecule to gold, which is apparent in the DFT-
computed deformation density. The theory and experiment agree that
there is $\sim 0.3$ V difference between the lower and upper pair of the sadded
pyrroles, and Fig. 3B visualizes this in the electrostatic field surface. This
intramolecular polarization was separately recognized through TERS

![Fig. 3. Results for CoTPP on Au(111): The $\Delta\nu$ maps in CH and CC mode are referenced to 2048.1 and 2046.9 cm$^{-1}$, respectively. (A) Atomically resolved forces due to hydrogen bonding between CO and the indicated H atoms. The indicated voltages are the potential differences relative to the gold substrate, as measured by the Stark shift of CO of 19.3 cm$^{-1}$/V according to the calibration of Fig. 1A. (B) Electrostatic field mapped on the isosurface of local density of states (LDOS). The common image size is 27 Å × 27 Å. The set point is 0.1 nA, 1.2 V.](image-url)
imaging of CoTPP with bare silver tips, where the Stark shift of a normal mode could be seen within the molecule (28).

The CH FWHM map of CoTPP appears as a stadium with two foci bounded by the molecular frame. We can also see partial edges of the recursion of the stadium at an inter-ring separation of ~9 Å, which, at $V_b = 1.2$ V, is consistent with the momentum of the surface Shockley state sustained on Au(111) (37, 40). We can see the secondary rings around both ZnEtio and CoTPP in expanded area scans (fig. S8). The ripples represent the dielectric response of the two-dimensional (2D) gas to the charge on the molecular adsorbates. This exquisite sensitivity to small fluctuations in surface charge density may be reconciled by the coulombic force exerted on the dangling charge on oxygen, sensed by motional instability of a very soft mode ($\kappa \rightarrow 0$), such as the azimuthal component of the 2D pendular motion. Such a motion would carry a magnetic field and could, in principle, serve as a molecular magnetometer.

**DISCUSSION**

The presented deployment of a single CO molecule as a sensor and transducer may be recognized as a leap towards the ultimate limit in miniaturization of MEMS in current use. In effect, TERS-enabled single-molecule vibrational spectroscopy directly accesses the electromechanical machinery of individual molecules. Under the more general framework of mfm, the present implementation has emphasized the scanning electrometer as a probe of electrostatic fields with submolecular spatial resolution. It gives access to electrostatic potential surfaces that define molecular shapes of greatest functional relevance, which, to date, have been mainly theoretical constructs. Electrostatic potentials distinguish the activity of surfaces and interfaces that control processes ranging from heterogeneous catalysis to optoelectronic devices, and to the extent that charge transfer drives the fundamental molecular processes, charge distributions on the nanoscale provide the structural information of functional relevance. Yet, for the most part, quantitative probes of electrostatics on the nanoscale have been lacking. The challenge is addressed with the single-molecule electrometer. The demonstrated quantitative measurement of charge on a physisorbed molecule, its intramolecular distribution and associated structural deformation, and surface dielectric response are fundamental to understanding interfaces, where the predictability of current theory remains questionable. Beyond probing fundamental science of interfaces, it is not too difficult to surmise that TERS-relayed single-molecule vibrational spectroscopy may serve as the essential, missing multimeter required to advance the field of molecular electronics.

**MATERIALS AND METHODS**

**Experimental**

STM-TERS measurements were performed under UHV (base pressure $= 4 \times 10^{-11}$ torr) at 6 K. A parabolic mirror installed inside the homebuilt STM system was aligned to the tip apex by imaging electroluminescence from the tunneling junction (41). For Raman measurements, the tip-sample junction was illuminated at 45° with a single-mode 634-nm diode laser (CrystaLaser) focused at the tunneling junction through an aspheric lens. The Raman spectra were acquired using a 0.3-m spectrograph (SpectraPro 2300i, Princeton Instruments) equipped with a liquid nitrogen-cooled charge-coupled device (Spec-10). The nanoscopically smooth silver tip was prepared by ex situ Ar+ field-directed sputter sharpening (FDSS) and finalized by Ne+ ion FDSS in situ (11). The cone radius of the tip before in situ processing was 16 nm. We dosed $^{12}$C$^{18}$O, CoTPP, and ZnEtio onto the Au(111) surface, as shown in fig. S1. The Ag tip was terminated by a single CO molecule through field emission on a CO lattice gas on Au(111), and the functionalization was directly verified through the CO stretch Raman spectrum and enhanced resolution in STM topographic images. The CO Raman maps were acquired in constant current and constant height modes.

**Theoretical calculations**

The geometry optimizations were performed using DFT at the Generalized Gradient Approximation (GGA)–Perdew-Burke-Ernzerhof (PBE) level, with the dispersion correction (DFT-D3) (42) on the ADF-BAND package (43, 44). The Slater-type orbitals represented by double zeta basis sets without polarization functions with small frozen cores were used. The relativistic effects were taken into account by means of the scalar zero-order regular approximation (45–47). The spin-unrestricted approach was used for the open shell system of CoTPP adsorbed on the Au(111) surface. During the structural minimizations, the Au slab was constrained to the bulk with the experimental lattice parameter of 4.08 Å to be consistent with the experimental adsorbate parameter (34). The CoTPP was placed on the top site with the orientation of 39.5° between N-Co-N axis and (110) direction of the face-centered cubic (111) surface.

To reduce the interplay effects arising from the molecules on the adjacent unit cells, the size of the unit cell was extended to $28.8 \times 29.9 \times 22.7$ Å in the electronic state calculations. The Au slab model consisted of 360 atoms in three layers. The plane-wave DFT calculations were carried out using the Quantum ESPRESSO package (48) to reduce the computational cost. The GGA-PBE functional incorporated with dispersion correction (DFT-D2) was used. We found that the combination of wave function cutoff of 80 rydberg (Ry) and charge density cutoff of 800 Ry, together with ultrasoft pseudopotentials, provided a reliable electron densities for the electrostatic field calculations. The spin-polarization calculations with the initial guess of 0.05 static magnetization were used for the CoTPP system.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/6/eaat5472/DC1

**Supplementary Materials and Methods**

Supplementary Text

fig S1. Topographic image of CoTPP, ZnEtio, and CO islands adsorbed on the Au(111) surface at 6 K.

fig S2. Schematic diagram and equivalent circuit.

fig S3. The vibrational Stark effect on CO.

fig S4. Coupling of two differentially terminated CO tips.

fig S5. Equivalent charge model for ZnEtio.

fig S6. Equivalent charge model for CoTPP.

fig S7. Variation of Raman resonance peaks.

fig S8. Detection of standing waves through the linewidth of CO stretch peak.

fig S9. Equivalent charge model for ZnEtio.

fig S10. Electrostatic potential, field, and CO frequency shift mapping of ZnEtio on the Au(111) surface.

fig S11. Electrostatic potential, field, and CO frequency shift mapping of the CoTPP on the Au(111) surface.

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