

presented here clearly shows the difference between the simple spectrum of the input (Fig. 2b) and the complex multi-hump spectrum of the output (Fig. 3e). During propagation, then, there is a **k**-space evolution in which energy transfers from regions of anomalous diffraction to regions of normal diffraction. Moreover, Fig. 4b and e clearly shows that energy transfers between bands. Because different **k**-vectors correspond to different Bloch modes, this energy transfer corresponds to an inherently nonlinear coupling between modes of the linear lattice. In this sense, our measurements are related to the Fermi–Pasta–Ulam problem³⁰. In the Fermi–Pasta–Ulam system, a lattice mode was excited, and it was expected that nonlinearity would redistribute the energy to a homogeneous state, that is, lead to equipartition. Instead, energy recurred to the initial mode, exhibiting energy oscillations between the initial mode and a finite group of modes, in an almost periodic fashion. In our system, an initially homogeneous **k**-space distribution evolves into a steady-state multi-humped soliton power spectrum. The focus of this Letter has been on the observation of these RPLs, but the rich dynamics underlying this energy transfer suggests many applications. For example, the spatially incoherent input beam can be used as a probe with given statistics, and the imaging techniques outlined here allow the observation of nonlinear effects, in both real and Fourier space.

Our experiments open up new possibilities in other nonlinear periodic systems beyond optics. For example, one can think of random-phase matter-wave lattice solitons in Bose–Einstein condensates, where the periodic potential is also optically induced. Similarly, one can envision random-phase solitons occurring with vibrational waves propagating along periodic molecular structures, finite-temperature plasma waves, or with charge-density waves in polymers or in crystalline conductors. In a more general sense, RPLs should exist in any nonlinear periodic system, because fluctuations (quantum, thermal, and so on) are always present and the propagating waves are never fully correlated. □

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Conversion of large-amplitude vibration to electron excitation at a metal surface

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Gaining insight into the nature and dynamics of the transition state is the essence of mechanistic investigations of chemical reactions¹, yet the fleeting configuration when existing chemical bonds dissociate while new ones form is extremely difficult to examine directly². Adiabatic potential-energy surfaces—usually derived using quantum chemical methods³ that assume mutually independent nuclear and electronic motion⁴—quantify the fundamental forces between atoms involved in reaction and thus provide accurate descriptions of a reacting system as it moves through its transition state^{5,6}. This approach, widely tested for gas-phase reactions⁷, is now also commonly applied to chemical reactions at metal surfaces⁸. There is, however, some evidence calling into question the correctness of this theoretical approach for surface reactions: electronic excitation upon highly exothermic chemisorption has been observed⁹, and indirect evidence suggests that large-amplitude vibrations of reactant molecules can excite electrons at metal surfaces^{10,11}. Here we report the detection of ‘hot’ electrons leaving a metal surface as vibrationally highly excited NO molecules collide with it. Electron emission only occurs once the vibrational energy exceeds the surface work function, and is at least 10,000 times more efficient than the emissions seen in similar systems where large-amplitude vibrations were not involved^{12–18}. These observations unambiguously demonstrate the direct conversion of vibrational to electronic excitation, thus questioning one of the basic assumptions currently used in theoretical approaches to describing bond-dissociation at metal surfaces.

Electronically adiabatic potential-energy surfaces computed with *ab initio* quantum chemistry methods have played a central role in advancing our understanding of chemical reactions. This powerful conceptual and predictive system is based on the assumption that nuclear motion associated with the reorganization of chemical bonds proceeds without facile electronic excitation (called the electronically adiabatic or Born–Oppenheimer approximation). Although this assumption has been widely tested for gas-phase reactions, less is known for reactions at metal interfaces.

Perhaps the greatest value of the electronically adiabatic potential-energy surface stems from its use in providing an accurate description of motion through a chemical transition state, given that experimental detection of chemical transition states is extremely difficult (see ref. 2 for a notable exception). Thus for most reactions, theory plays an essential role in revealing their fundamental nature.

Motion through a transition state involves large-amplitude vibration: bond elongation is so extreme that dramatic changes occur in the structure of the electronic cloud holding the atoms together as the system reorganizes to new chemical species. There is already indirect evidence that under these conditions, heavy-atom vibrational motion can exchange large amounts of energy, producing electronic excitations in a metal, which casts doubt on the electronically adiabatic picture of chemical transition states for reactions at metal interfaces^{10,11}. As yet, however, there are no direct observations of ‘hot’ electrons produced by excitation exchange with large-amplitude vibration.

Here we report experiments intended to demonstrate the importance of non-adiabatic electronic effects associated with large-amplitude intramolecular motions similar to those associated with transition-state traversal. To carry out this work, we used an apparatus similar to that of ref. 19. A pulsed molecular beam containing NO with a kinetic energy of 29 meV is formed in the ‘source’ vacuum chamber. It then passes through a skimmer into another ‘excitation and detection’ vacuum chamber, where it is resonantly excited with laser light to prepare selected quantum states in high vibrational levels. This chamber also provides a laser-induced fluorescence (LIF) detection station for monitoring the intensity of the beam of vibrationally excited molecules. After passing through a 1-mm aperture into an ultrahigh-vacuum surface science chamber, the molecules collide with the metal surface,

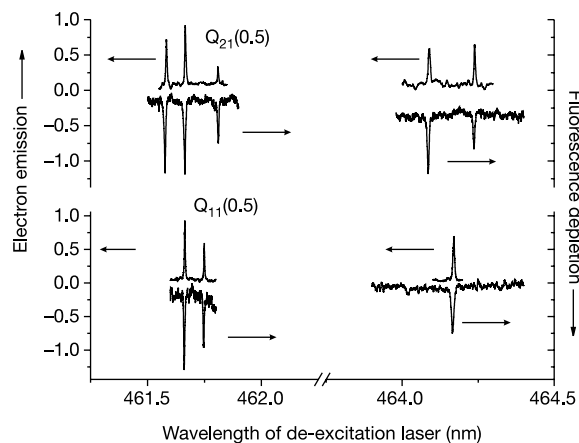


Figure 1 Electron emission from NO($\nu = 18$) collisions with Cs/Au(111) surface. Electron emission (up-going signal) is detected as a function of the de-excitation laser’s wavelength for two excitation transitions ($Q_{21}(0,5)$ and $Q_{11}(0,5)$). We compare these spectra to fluorescence depletion (down-going signal) spectra observed under identical conditions. The observed spectral resonances agree with known transitions of the $A^2\Sigma^+(\nu' = 3)$ to $X^2\Pi(\nu = 18)$ system of NO to better than the line-width of the laser.

inducing emission of electrons. Stimulated emission pumping²⁰, SEP(ν), was used to produce NO molecules in a selected excited vibrational states, ν , where $18 \geq \nu \geq 4$. This was accomplished through excitation of NO to the excited electronic state $A^2\Sigma^+(\nu' = 3)$ followed by laser-induced de-excitation to the targeted vibrational state, ν , back in the ground ($X^2\Pi$) electronic state. We also used spontaneous emission from laser-prepared $A^2\Sigma^+(\nu = 0)$ to populate vibrationally excited states, $X^2\Pi(\nu \leq 5)$.

To obtain the relative electron emission signals for different vibrational states, we compared the signal produced by the SEP-prepared state to the residual signal produced in the absence of the de-excitation laser, where vibrational states are populated by spontaneous emission from $A^2\Sigma^+(\nu' = 3)$. This provided an internal standard of electron emission that allowed us to gain a measure of control over the day-to-day reproducibility of the experiment.

To determine the per-collision efficiency for electron emission, the absolute number of NO(ν) molecules in the molecular beam pulses was determined from saturated laser-induced fluorescence detection at the position where the beam collides with the surface. The absolute number of fluorescence photons was derived from the observed current of a solar-blind photomultiplier tube, accounting for: (1) measured photomultiplier gain, (2) photocathode quantum efficiency, (3) optical collection efficiency of the lens system, and (4) spatial overlap of the laser and molecular beams. Emitted electrons were counted with a multi-channel scaler.

We prepared low-work-function surfaces by depositing Cs on Au(111) with a commercially available source (SAES Getters) in a ultrahigh-vacuum chamber with base pressure of $\sim 1 \times 10^{-10}$ torr. The surface temperature was ~ 300 K in all the experiments reported here. The work function of various metals with submonolayer Cs

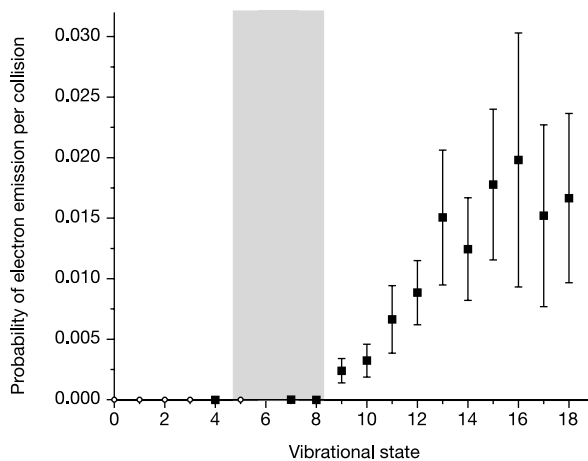


Figure 2 Vibrational dependence of electron emission efficiency. Stimulated emission pumping (solid squares) and spontaneous emission from the $A^2\Sigma^+(\nu = 0)$ state (open circles) lead to relative electron emission probabilities for the indicated vibrational states. The points are average values of at least five measurements for each value of ν . The error bars reflect an analysis of error propagation from measured uncertainties in factors contributing to the derived quantum yield. These include uncertainties in excitation and de-excitation efficiency. These error bars are similar to 90% confidence intervals (using Student’s *t*-test) derived from statistical analysis of multiple measurements. For $\nu = 13$ and 16, laser de-excitation is accompanied by some absorption out of the excited electronic state. This does not contribute to the electron emission signal but increases the error in the measurement. Experiments producing $\nu = 6$ were not technically feasible. Error bars for data indicated by open circles are smaller than the symbol. The shaded region indicates the vibrational equivalent of the surface work function ($\nu = 6$ and 7 correspond to 1.34 and 1.55 eV, respectively).

coverage drops below the asymptotic work functions of both the base metal and pure Cs^{17,21–23}. We monitored the effect of Cs dosage on the work function by observing the photoemission generated by a He-Ne laser ($h\nu = 1.96$ eV), which enables us to prepare surfaces that exhibit maximum photoemission and thus a surface near the work function minimum²². Cs-covered gold surfaces prepared in this way have work functions between 1.3 and 1.6 eV (ref. 21).

We detected emitted electrons with a 40-mm double micro-channel-plate detector located close to the surface and identified the observed signals as electrons by the fact that a 2–3-gauss magnetic field effectively removes the signal. The angle of incidence between the molecular beam and the surface normal was fixed at 60° to maximize electron collection.

Figure 1 shows the results observed when monitoring the electron current emitted from the surface, while scanning the de-excitation laser wavelength (upward-going signals) in the SEP ($\nu = 18$) pumping scheme. Resonances in the depletion of side fluorescence²⁰ were measured simultaneously at the preparation zone. These are also shown in Fig. 1 (downward-going signals). There is a one-to-one correspondence between electron emission and fluorescence depletion resonances, establishing that incident NO ($\nu = 18$) is responsible for the observed electron signal. The observed resonance wavelengths can be predicted from spectroscopic theory of the NO molecule to better than the bandwidth of the laser (0.12 cm⁻¹).

Collisions of NO (ν) with low-work-function surfaces resulted in electron emission for $\nu = 9–18$. States higher than $\nu = 18$ were not studied. Tuning the laser away from either of the two resonances (excitation and de-excitation) used for state preparation resulted in a reduction or complete loss of electron emission. SEP was also used to prepare NO ($\nu = 4, 5$, and 7), resulting in no detectable electron emission. NO ($\nu = 8$) was prepared and sometimes yielded a non-zero emission signal. Spontaneous emission from NO- $A^2\Sigma^+$ ($\nu = 0$), which produces molecules in vibrational states $\nu \leq 5$, also gave no electron emission. No electron emission was observed for NO in its ground vibrational state. No surface oxide was required to observe the electron emission, indicating a mechanism of electron emission different from previous reports of exoelectron emission resulting from NO ($\nu = 0$) interactions at surfaces^{16–18}.

The vibrational dependence of the per-collision electron emission efficiency is shown in Fig. 2. For comparison, the energetic equivalent position of the surface work function is shown as a grey-shaded bar. We see a vibrational threshold near the energetic equivalent of the surface work function, strong evidence that we are witnessing direct conversion of vibrational energy to electronic excitation in the metal. These results indicate a yield of approximately 0.02 electrons per incident NO ($\nu = 18$) molecule. By comparison, we note that the yield previously observed for exoelectron emission from ground vibrational state NO, O₂, N₂O and NO₂ on Cs and Li films is of the order of 10⁻⁸ to 10⁻⁶ (refs 12–18).

A detailed mechanistic explanation for the experimental observation of electron emission induced by large-amplitude molecular vibration will require interactions between theory and additional experimental work, but some aspects of the dynamics already seem clear. First, it seems unlikely that we are witnessing electron emission resulting from NO dissociation. Greber¹² has described how a 'hole' on a newly formed O⁻ ion formed after dissociative electron transfer may plummet in energy far below the Fermi level before an additional electron is transferred to produce the ground electronic state O²⁻. The quenching of this hole can result in an Auger emission event. In such an O⁻ 'chemical hole diving' process, electron emission efficiencies of 10⁻⁶–10⁻⁸ were reported^{15,16}, whereas here we observed efficiencies as high as 0.02. Furthermore, such a dissociative mechanism could not explain the observed vibrational threshold, without invoking a coincidental dissociation barrier equal to the work function.

It also seems unlikely that the vibrational energy transfer proceeds in a fashion where single vibrational quanta are transferred efficiently but sequentially in multiple steps. In this case, the vibrational energy would transfer in small amounts to many electrons and it is unlikely that any single electron would acquire energy beyond the work function. Indeed, the observation of a vibrational energy threshold for electron emission near the value of the surface work functions indicates that multiple vibrational quanta are coupled to a single electron, a conclusion that is easily reconciled with a mechanism where an electron is transferred transiently to the NO molecule.

Thus, the considerations presented above strongly suggest that the observed electron emission results from a process that converts large-amplitude vibrational energy of heavy nuclei in the vicinity of the metal surface to translational energy of a metal electron by a mechanism involving electron transfer from the metal to the NO molecule. The observation that large-amplitude vibrational motion can efficiently excite metallic electrons by more than 1.3 eV points to the need to account for strong electronically non-adiabatic influences in theories of chemical reactions at metal interfaces. □

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