

Single-Molecule Infrared Spectroscopy with Scanning Tunneling Microscopy

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Abstract: Probing vibrations at single-molecule level is essential for achieving bond-specific chemical control in realistic heterogeneous environments. Here, we introduce a new measurement scheme integrating frequency-tunable infrared excitation with scanning tunneling microscopy to characterize vibration-mediated nuclear motions of single molecules. We first validated the technique by monitoring the infrared-induced rotation of the ethynyl radical and then applied it to mapping pyrrolidine's conformational dynamics. The resulting broadband spectra captured fundamental vibrational modes together with rich overtone and combination bands inaccessible by conventional methods, confirmed with isotopic substitutions. Density functional theory calculations showed that delocalized modes coupled with pyrrolidine ring puckering drive the structural transition, revealing altered selection rules compared to traditional infrared spectroscopy. This new experimental platform enables probing of molecular vibrations and transformations with atomic precision.

Main Text:

Interest in molecular vibrations has been central to chemistry for well over a century. Vibrational characterization remains a fundamental tool for probing molecular structure and reaction dynamics (1). Meanwhile, directing energy into a single, highly excited chemical bond for a sustained period holds great promise for externally manipulating chemical reactivity with bond specificity (2). Many such strategies have proven unrealistic, largely due to the inhomogeneity of molecular interactions within ensemble environments. However, by carefully engineering the local interactions of a single molecule with its nanoscale surroundings, new opportunities emerge for achieving vibrationally induced control over chemical behavior. Realizing these potential calls for vibrational characterization and manipulation with molecular-scale resolution. Traditional infrared (IR) techniques, despite their power in non-destructive molecular fingerprinting, are restricted by the optical diffraction limit to the micron scale. This constraint, combined with the small IR absorption cross-section of individual molecules compared with the pronounced thermal noise in mid-infrared detectors (3), necessitates ensemble rather than single-molecule measurements. Consequently, key nanoscale molecular characteristics—including site-specific vibrational signatures (4), environmental interactions (5, 6) and population heterogeneity (7), are obscured. Uncovering these details is essential for elucidating elementary steps in surface catalysis (8-10), revealing electron-phonon (11, 12) and intramolecular vibrational coupling mechanisms (2). Achieving single-molecule vibrational resolution remains a transformative goal in chemistry. One direction toward this goal involves purely optical methods that maximize signal-to-noise through extreme isolation or enhanced vibrational cross-sections, including matrix-isolation spectroscopy (13), ion trap tagging spectroscopy (14), surface-enhanced Raman scattering (15, 16), and ultrasensitive visible-mediated mid-IR detection (17). However, these approaches all lack the microscopic resolution needed to characterize a molecule's internal structure.

Scanning tunneling microscopy (STM) offers a naturally advantageous platform for single-molecule studies through its atomic-scale spatial resolution. Over four decades since its inception, vibrational spectroscopy with STM has advanced along two primary paths. STM tip-enhanced Raman spectroscopy (STM-TERS) harnesses the plasmon resonance enhancement of the tip for nanoscale molecular vibration detection (18-20), while inelastic electron tunneling spectroscopy (STM-IETS) (21), as well as its derivative STM action spectroscopy (22), excites single-molecule vibrations through inelastic electron tunneling. However, each method presents distinct limitations. STM-TERS, despite demonstrated high localization from the enhanced near-field at the tip apex, exhibits signal strength strongly dependent on plasmon resonance conditions including tip material, geometry, and sample dielectric properties (23). It also relies on inelastic photon scattering which requires a change in molecular polarizability. STM-IETS, although possessing exceptional spatial resolution inherent with electron tunneling, suffers from energy resolution limited by thermal broadening and electronic noise (24). Its selection rules—dictated by how vibrations modulate the tunneling matrix element—differ from optical spectroscopy and remain underexplored. Moreover, competition between elastic and inelastic tunneling and weak electron-vibration coupling at higher energies (25, 26) limits IETS signal intensity, restricting broad spectral coverage.

In contrast to both TERS and IETS, combining IR excitation with tunneling current detection with STM, termed infrared integrated STM (IRiSTM), functions as a resonant absorption technique with clearer selection rules, potentially offering a more complete molecular vibrational fingerprint. Despite this seemingly straightforward concept, progress has been slow. The most well-known advance dates to 2013, when Crommie et al. (27) detected molecular vibrational

spectra via IR-induced thermal expansion of a gold substrate. However, this detection relies on photothermal response of the substrate instead of the molecule, therefore failing to achieve molecular-level resolution. Single-molecule IR spectroscopy with STM remains a long-sought-after goal among chemists.

Results and Discussion

The strong IR absorption of common vibrational modes (e.g., C–H and N–H stretching) suggests molecular responses to IR excitation should, in principle, be detectable. The key lies in developing a sufficiently localized and sensitive detection scheme relying on the photon-induced change to the tunneling current (28, 29) — an approach that shares a similar detection mechanism with STM-IETS and STM-based action spectroscopy (22, 30). Specifically, IR-induced vibrational excitation modulates junction conductance either by perturbing the molecule's intrinsic structure or molecule-environment interactions (31), measurable through either direct amplitude changes or with phase-sensitive lock-in detection, providing a highly localized probe of absorption processes. Importantly, this scheme relies on tunneling current detection rather than scattered light, bypassing the stringent tip plasmonic requirements in TERS. At the same time, vibrational excitation via direct photon absorption offers a much larger cross-section than electron scattering, overcoming the key limitation of IETS. Together, these advantages enable the potential detection of subtle vibrational features, such as weak overtone transitions with molecular resolution.

Building upon these principles, we demonstrated the first single-molecule-level IRiSTM relying on global IR excitation and in situ tunneling current detection on two distinct molecular systems, ethynyl (C_2H) radical as a minimal testbed and pyrrolidine ($\text{C}_4\text{H}_9\text{N}$) for enhanced structure complexity. The experimental set-up integrated wavelength-tunable femtosecond IR pulses with a cryogenic STM under ultrahigh vacuum (UHV) conditions, enabling real-time tracking of the conformational dynamics of individual molecules (Fig. 1A). Details about the experimental set-up and measurement approaches are presented in the Supplementary Materials (SM) sections 1.1-1.3. Two IR triggered current signals, vibrational-mediated structural transition rate and photo modulated tunneling current, are measured to characterize the molecular vibration with Angstrom scale resolution.

The C_2H radical is chosen as one of the simplest alkynyl species for surface-adsorbed radicals. Its triatomic simplicity ensures its vibrational modes, primarily the C–H stretch and the C=C stretch, are sparse, well-defined, and have been studied in the gas phase or surface adsorbates for unambiguous assignment (32, 33). Compared to other more symmetrical alkynes such as acetylene (C_2H_2), the non-planar adsorption geometry of C_2H on Cu(100) (SM Fig. S9A-B) ensures its IR activity is not being frustrated by surface selection rules (34). The C_2H radical adopts four equivalent adsorption configurations aligned with the underlying Cu(100) lattice symmetry, as revealed by sequential STM imaging (Fig. 1A-B), in good agreement with the density functional theory (DFT) simulation (Fig. 1A Inset). Upon IR excitation between 1.3 and 6.3 μm , the molecules underwent photo-excited in-plane rotation among these four adsorption configurations, observed as four tip height levels (ΔZ) under constant-current mode (Fig. 1C).

Previous studies have revealed that the C_2H rotation on Cu(100) is mediated by its vibrations (21, 35). Based on this relationship, we measure the rotational rate, defined as the number of transition events per 1 M laser pulses at a calibrated photon flux, as a function of the incident light wavelength under identical conditions (temperature, bias/current, tip-sample distance, refer to SM sections 1.2 and 2.5), to generate the energy resolved vibrational action spectra of C_2H and its deuterium substituted isotopologue C_2D (Fig 1D). C_2H spectrum (blue) displayed a prominent

fundamental C–H stretching $\nu(\text{C–H})$ peak at 3169 cm^{-1} , as well as its first overtone, $2\nu(\text{C–H})$, at 6311 cm^{-1} . Additionally, the fundamental $\nu(\text{C=C})$ stretching mode is resolved near 1600 cm^{-1} . The identities of these vibrational modes are unambiguously confirmed by comparison with the C_2D spectrum (olive). As expected from the increased reduced mass, the C–D stretching fundamental $\nu(\text{C–D})$ is red-shifted to 2325 cm^{-1} , with its first overtone $2\nu(\text{C–D})$ at 4750 cm^{-1} and its second overtone $3\nu(\text{C–D})$ at 6872 cm^{-1} . These isotope-dependent shifts, together with the coincidence of the rotation rate maxima with the molecular vibrations, establish IRiSTM as a new vibrational spectroscopy for probing single-molecules on surfaces.

Having validated our experimental approach, we turned our focus to pyrrolidine, a system of more profound biological importance. Pyrrolidine is a prototypical cyclic secondary amine (36) that serves as the core cyclic structure in amino acid proline, often referred to as the “proline kink”. Its transition between the equatorial and axial isomers poses severe steric constraints that have direct consequences for protein folding, stability, and dynamics (37). Here, we deposited a low coverage of pyrrolidine onto Cu(100) surface held at 6.3 K to render intermolecular interactions negligible (38, 39) (Fig. 2A–B). Molecules adsorbed via nitrogen lone pair electrons exhibited two distinct conformational states, easily differentiated by their apparent heights (Figs. 2C–E) (40–43). These two conformers are denoted as the “Low” (Fig. 2C, $0.9\text{ \AA}$ apparent height, matching the gas-phase equatorial isomer) and “High” states (Fig. 2D, $1.5\text{ \AA}$ apparent height, corresponding to the axial isomer). The highly symmetric STM images in both states suggested continuous in-plane rotation between four equivalent adsorption geometries, reflecting the underlying Cu(100) surface's four-fold symmetry (44). Low rate of spontaneous transition between two states (approximately 0.1 Hz), driven by enhanced anharmonic vibration–phonon coupling instead of electron or photon excitation (45), were observed during scanning, as exemplified by the captured occasional transitions shown in Fig. 2F with bias set to 20 mV .

In the absence of laser excitation, the pyrrolidine predominantly resides in the “High” state. However, under $\lambda = 2.66\text{ }\mu\text{m}$ irradiation, it rapidly switches between two structures (Fig. 2F, bottom). As with C_2H , this structural transition is mediated by pyrrolidine vibrations. Accordingly, we obtained a vibrational spectrum by measuring the switching rate between the “High” and “Low” states over the $1.3\text{--}6.3\text{ }\mu\text{m}$ wavelength range. The resulting spectrum (Fig. 3A) featured more complex vibrational resonances than those of ethynyl and of its isotopologue.

To elucidate the nature of these resonances, we compared their energies with known vibrational modes in the literature (46) as well as the Fourier transform infrared spectra (FTIR) of pyrrolidine in both thin films and sub-monolayer coverage on copper surfaces (Fig. S5), and identify them as fundamental, overtone, or combination modes—primarily involving N–H and C–H stretches as well as the ring deformation modes. For instance, fundamental $\nu(\text{N–H})$ appeared at 3225 cm^{-1} , and overtones near 5920 cm^{-1} and 6250 cm^{-1} corresponded to $2\nu(\text{C–H})$ or $2\nu(\text{N–H})$. Of particular interest is the intense feature between 4500 and 4800 cm^{-1} , which was assigned to combination modes involving higher-order vibrational overtones (up to fourth order) concerning the motion of the five-membered ring (SM Fig. S15 and Table S3), indicating exceptionally strong coupling between these vibrations and the switching coordinate. The prominent signal observed at 3600 cm^{-1} was assigned to a combination mode of N–H stretching with Cu–N bending ($\sim 42\text{ meV}$, 344 cm^{-1}), where the Cu–N bending has previously been established as the primary vibrational mode mediating the structural transition (39, 44).

Alongside the switching rate measurements, we monitored the fraction of time the molecule occupied the “High” state—defined as $\frac{t_{\text{High}}}{(t_{\text{High}} + t_{\text{Low}})}$, as a function of photon energy (Fig. 3B), where

t_{High} and t_{Low} represent the total residence time of the molecule in “High” and “Low” states respectively. Because photoexcitation promoted “High-to-Low” transitions, “High” state population decreased significantly when exciting certain vibrations including the $\nu(\text{N-H})$ at 3225 cm^{-1} , the combination mode at 3600 cm^{-1} , and the first C-H stretch overtone $2\nu(\text{C-H})$ at 5920 cm^{-1} . These occupation measurements provided complementary insight to the switching rates: changes in the “High” state population reflected differences in the alignment between the vibrational dipoles relative to the IR polarization in the two conformers. If the orientation change reduces the IR absorption cross-section in the “Low” state, the “Low-to-High” transition will be suppressed. As a result, the molecule resided longer in the “Low” state. In contrast, switching mediated by delocalized ring modes between $4500\text{--}5500\text{ cm}^{-1}$, despite showing a more pronounced enhancement in the switching rate, resulted in only minor changes in the occupation ratio. This feature was likely due to the relatively small difference in IR absorption cross-section between the two conformers for these vibrations (also see SM sections 2.12-13).

For surface-adsorbed molecules, multiple adsorption structures with similar energies commonly coexist. As a result, vibration-mediated transitions, either between conformers (e.g., pyrrolidine) or among equivalent adsorption geometries (e.g., C_2H), should occur generally in principle. In reality, these transitions are often too fast for STM to resolve, leaving the measured tunneling current as an average over multiple states. This motivates a more general approach based on directly detecting photon-induced tunneling currents instead of switching rates. To this end, we also obtained the vibrational spectrum of pyrrolidine by measuring the IR modulated current as a function of laser wavelength using a lock-in technique at elevated laser power. In this measurement, the laser was chopped at 84 Hz , and the photocurrent was detected with a lock-in amplifier synchronized to the chopper. Because power modulation induces large background oscillations from tip thermal expansion, we applied a synchronous, phase-matched oscillation to the tip piezo to actively damp this motion (28) (technical details in SM section 1.3). This scheme effectively suppresses background signals on $\text{Cu}(100)$, enabling clean photocurrent detection highly localized on the molecule (Fig. 3D, E). Using this method, we resolved vibrational features (Fig. 3C) consistent with those obtained from the switching-rate measurement (Fig. 3A), including peaks at the $\nu(\text{N-H})$, $2\nu(\text{C-H})$, and 3600 cm^{-1} combination band. However, the higher applied laser power, necessary to achieve a sufficient signal-to-noise ratio, also induced rapid in-plane molecular hopping when exciting vibrational modes that involve substantial lateral motion of the carbon atoms (e.g., the 4700 , 6360 , 6460 , and 7150 cm^{-1} combination modes), preventing data acquisition in the gray-shaded wavelength regions of Fig. 3C. Nonetheless, the close correspondence between photocurrent peaks and molecular modes establishes this as a broadly applicable scheme for single-molecule IR spectroscopy.

It is notable that the fundamental $\nu(\text{C-H})$ mode, though prominent in the IRiSTM spectrum of C_2H , was absent in pyrrolidine, despite being clearly resolved in both FTIR (Fig. S5) and STM-IETS (Fig. S6). This underscores that IRiSTM follows different selection rules from those in photon-absorption-based FTIR and electron-scattering-based STM-IETS. First, the vibration must be IR-active so that the molecule can be driven by the incident light. Second, vibration must induce measurable nuclear motion, either as a resolvable structural transition or a modification of the time-averaged tunneling current signal. The first criterion resembles IR excitation in a plasmonic or metallic cavity (47, 48), whereas the second is less well understood. To understand how different IR-excited vibrational modes couple to the pyrrolidine structural transition, we consider the framework defined by Sudden Vector Projection theory, which extends the Polanyi’s rule by quantitatively describing how vibrational motions aligned with the reaction coordinate can efficiently promote the reaction (49, 50). Based on this framework, we performed DFT normal-

mode analysis by projecting the vibrational displacement (sudden vectors) onto the reaction coordinate of “High-to-Low” switching (50). Detailed analysis is included in the SM sections 2.6-2.8 and Figs. S10 and S15. This analysis highlighted the vibrational modes that readily transfer energy to drive motion in the ring-puckering reaction coordinate (SM sections 2.3, 2.6-2.8). Correlation between the DFT with experimental results yielded highly consistent peak-to-mode assignments for the measured spectrum (SM Table S3). The result naturally explains the absence of the $\nu(\text{C-H})$ mode in the IRiSTM spectrum of pyrrolidine: this mode neither directly distorted the ring along the reaction coordinate nor coupled efficiently via intramolecular vibrational redistribution (IVR) to other vibrations with large-amplitude ring deformations. In the meantime, the well-known one-stretch to two-bend coupling of $\nu(\text{C-H})$ provided a fast energy dissipation channel (51). On the contrary, the substantially larger nuclear displacement and natural anharmonicity associated with the higher-quantum overtones (e.g., the first overtone $2\nu(\text{C-H})$) allowed them to contribute more efficiently to the conformational switching dynamics.

The pyrrolidine vibrations observed in IRiSTM were further confirmed by their isotope-dependent energy shifts. To facilitate direct comparison under identical experimental conditions, we co-deposited pyrrolidine, N-deuterated pyrrolidine (Pyrro N-D), and C-perdeuterated pyrrolidine (Pyrro D8). Although these isotopologues exhibited nearly identical topography (Fig. 5A), they were readily distinguished by distinct vibrational signatures. For example, a strong fundamental $\nu(\text{C-D})$ peak was observed at 2034 cm^{-1} for Pyrro D8 (Fig. 4A), and a weaker, but reproducible $\nu(\text{N-D})$ peak appears at 2300 cm^{-1} for Pyrro N-D (Fig. 4B). The downshift of $\nu(\text{C-D})$ brought its energy into resonance with ring-deformation modes, opening efficient IVR channels to reaction-coupled vibrations that $\nu(\text{C-H})$ could not access. Similar shifts were seen in the corresponding overtone and combination modes (Figs. 4C, D). Additionally, heavier isotopes have reduced vibrational amplitudes and couple weaker with the reaction coordinate, appearing as reduced switching for deuterated isotopes between 4500 and 5500 cm^{-1} , corresponding to the ring deformation modes, following the order: pyrrolidine > Pyrro N-D > Pyrro D8 (additional discussion in SM section 2.8).

Based on these specific vibration fingerprints, we could easily distinguish these isotopologues microscopically by tuning the IR frequency to resonate with specific X-H or X-D ($\text{X} = \text{N}$ or C) stretching vibrations. Irradiation resonant with the $\nu(\text{N-D})$ selectively activated the Pyrro N-D, leading to stripe-like features in the STM topography, clearly differentiated them from neighboring molecules (Fig. 5C). Similar selectivity was seen at $\nu(\text{C-D})$ for Pyrro D8 (Fig. 5B), $\nu(\text{N-H})$ for pyrrolidine or Pyrro D8 (Fig. 5E), and $2\nu(\text{C-H})$ for pyrrolidine or Pyrro N-D (Fig. 5F). This microscopic selectivity confirmed our vibrational mode assignments and highlighted IRiSTM's capability for rapid single-molecule chemical identification.

Conclusion

In conclusion, we have developed a broadband IRiSTM platform integrating wavelength-tunable femtosecond IR excitation with cryogenic UHV-STM to directly record the infrared excited vibrational spectrum of single ethynyl radicals and pyrrolidine molecules on Cu(100), filling a critical gap in single-molecule optical spectroscopy within scanning probe microscopy. By measuring IR-induced enhancements in the ethynyl rotation or pyrrolidine conformational switching rate across a broad spectral range, we obtained the first single-molecule IR spectra that revealed fundamental, overtone, and combination bands of both molecules. Selective deuteration (C_2H vs C_2D , and pyrrolidine vs Pyrro N-D and Pyrro D8) provided unambiguous mode assignments and enabled rapid chemical identification at the single-molecule level. DFT normal-mode projections onto the reaction coordinate, together with observed kinetic isotope effects,

demonstrated that the modes strongly coupled with the switching coordinate contribute more prominently to the measured conformational transition, providing selection rules that differ from both the traditional FTIR and the STM-IETS. Extending the measurement from photon-induced action rates to direct detection of IR modulated tunneling current further demonstrates the broader applicability of this technique. These results establish broadband IRiSTM as a powerful approach for single-molecule vibrational spectroscopy, real-time conformational dynamics, and in situ chemical identification at the atomic scale.

References and Notes

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Data and Materials Availability: The raw and processed data of this study are available for download (52). Other data needed to evaluate the conclusion in the paper are presented in the paper or the Supplementary Materials.

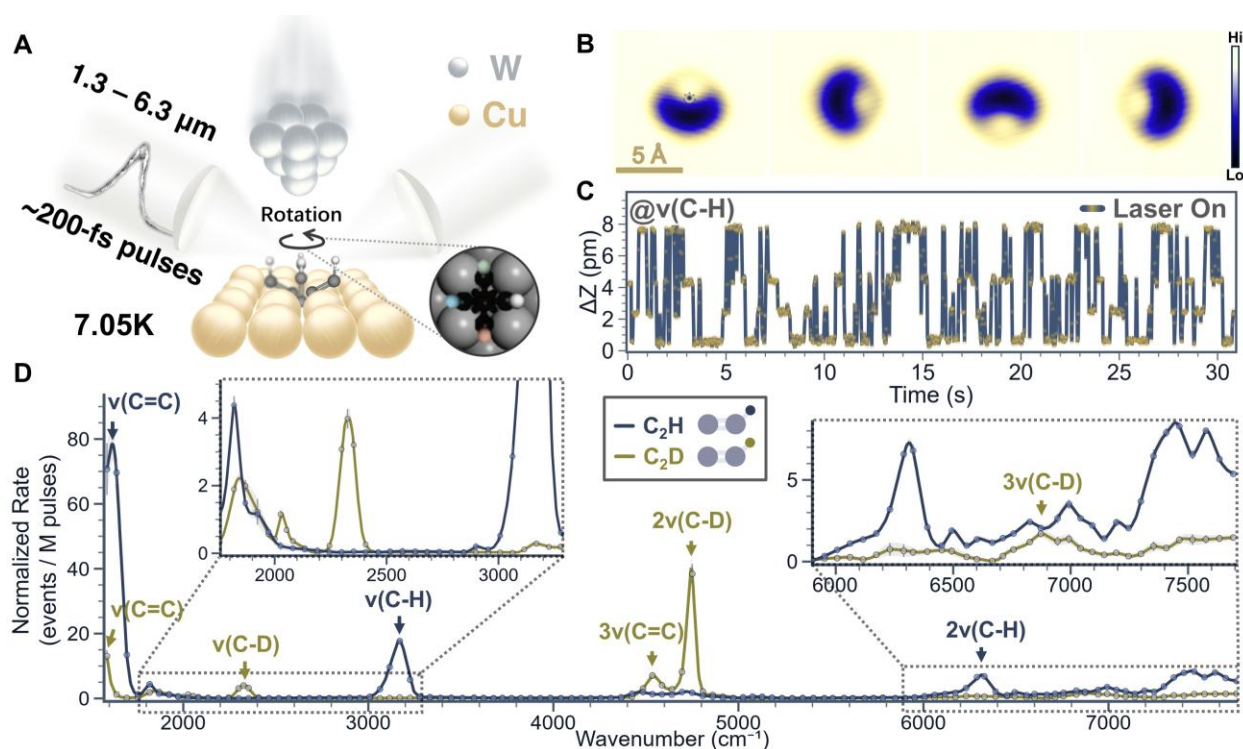


Fig. 1. IR-induced rotation of single ethynyl. (A) Schematic of the IRiSTM measurement. Tunable femtosecond mid-IR pulses (1.3–6.3 μm , ~ 200 fs) are focused into an STM junction held at 7.05 K to drive the rotation of an adsorbed ethynyl molecule. The inset shows four equivalent ethynyl adsorption configurations aligned with the Cu(100) lattice, as obtained from DFT simulations. (B) Sequential STM images of C_2H on Cu(100) ($V_b = 30$ mV, $I = 20$ pA), revealing four equivalent adsorption conformations. (C) Tip height (ΔZ) versus time trace ($V_b = 30$ mV, $I = 20$ pA) acquired with the laser tuned in resonance with the $\nu(\text{C-H})$ mode, showing rapid rotation of C_2H among the four orientations. The asterisk in (B) marks the tip position used for this measurement. (D) Vibrationally mediated rotation rate for C_2H (blue) and its deuterated isotopologue C_2D (olive) measured between 1587 to 7700 cm^{-1} . Error bars represent the 99% confidence interval (CI), calculated from $N = 36$ measurements. Colored solid lines are interpolation curves provided as a guide to the eye and were constructed directly from the raw discrete data points (grey dots).

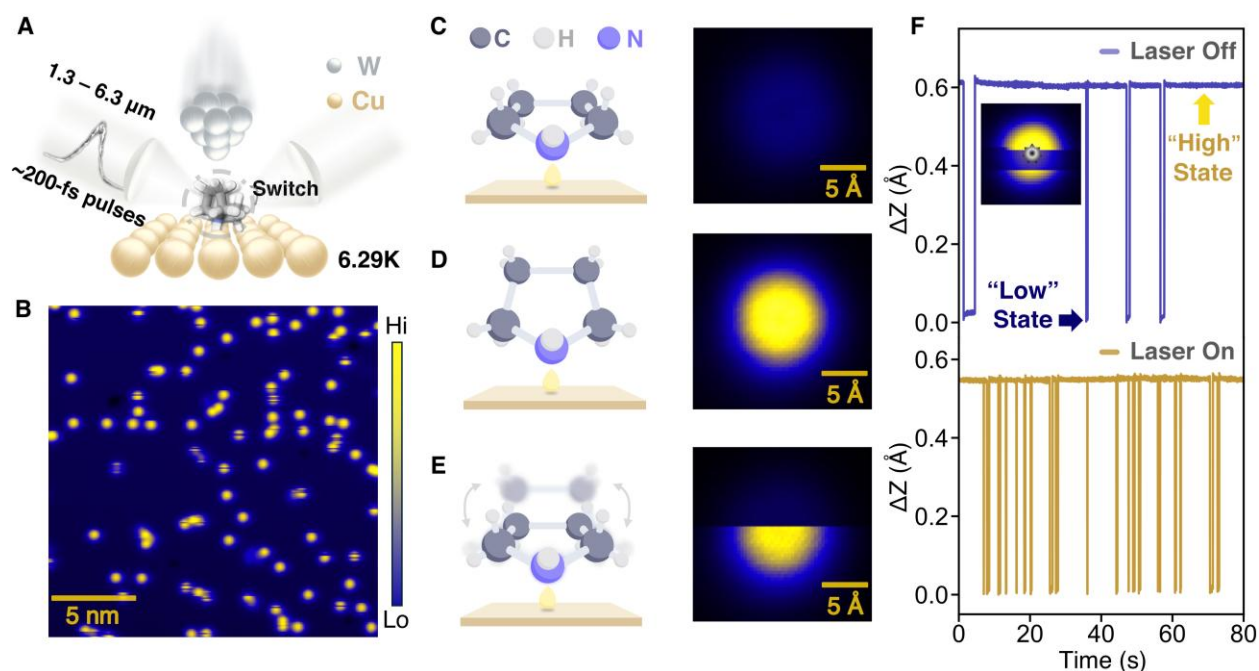


Fig. 2. IR-induced structural transformation of single pyrrolidines. (A) Schematic of IR excited conformational switching of a pyrrolidine molecule adsorbed on Cu(100). (B) STM Topography image of surface-adsorbed pyrrolidines ($V_b = 20$ mV, $I = 20$ pA). (C-E) Simulated front-view (left) and corresponding constant-height STM images (right) of pyrrolidine in “Low” (C) and “High” (D) conformations. The image in (E) captured a “High-to-Low” transition during scanning. (F) Tip height (ΔZ) versus time traces ($V_b = 20$ mV, $I = 20$ pA) showing bistable switching with laser off (top, 0.1 Hz) and under laser illumination at $\lambda = 2.66$ μm (bottom, 0.8 Hz). The asterisk in the inset image marks the tip position of the measurements.

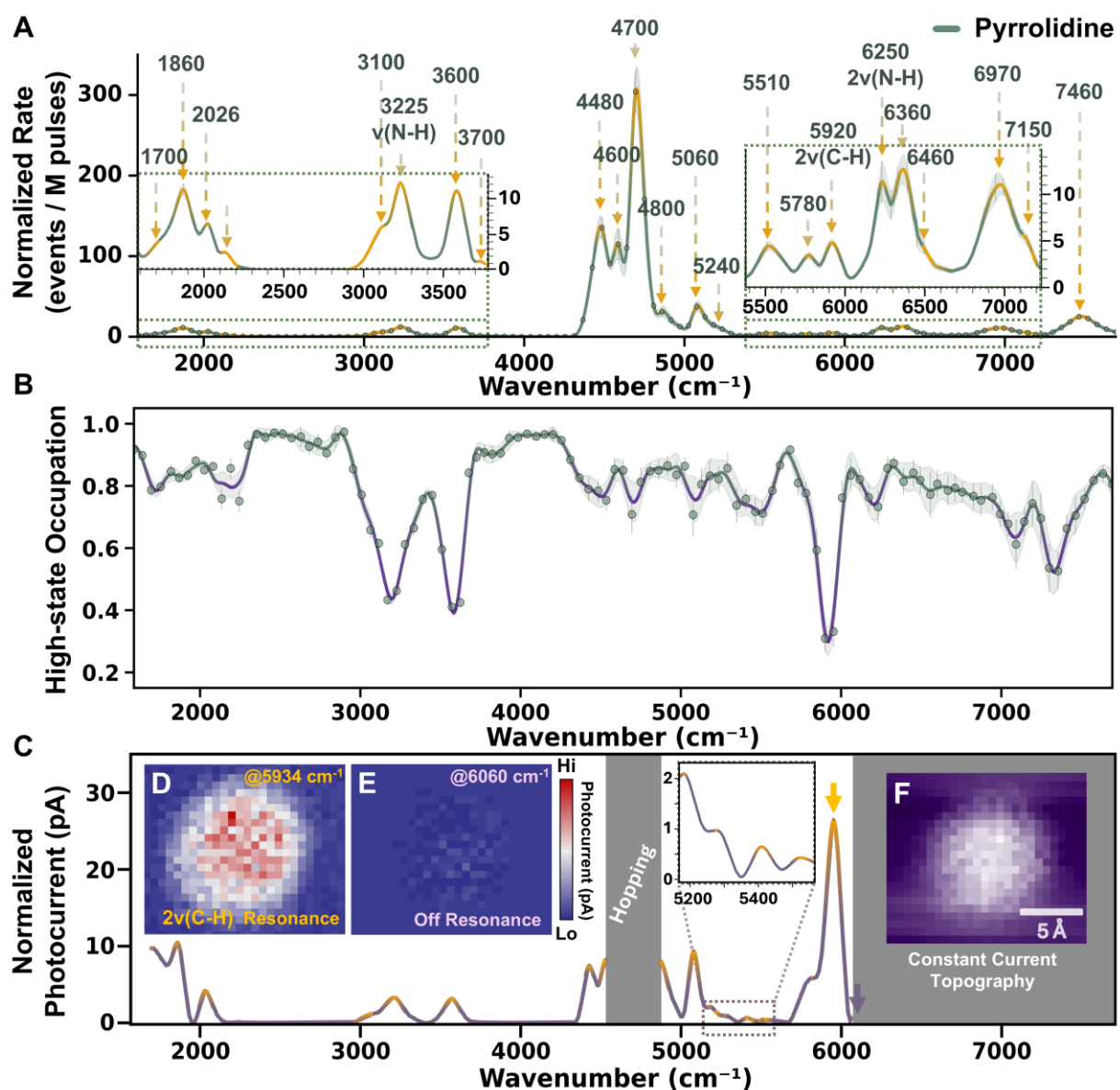


Fig. 3. Wavelength dependence of IR-induced conformational switching of pyrrolidine. (A) Vibrationally mediated switch rates of pyrrolidine measured over the range 1587-7700 cm^{-1} . Identified vibrational modes are indicated with arrows and highlighted in orange. Insets show enlarged views of lower intensity features. (B) “High” state occupation ratio ($\frac{t_{\text{High}}}{t_{\text{High}}+t_{\text{Low}}}$) as a function of wavenumber. Dips correspond to vibrational modes that preferably drove the “High-to-Low” transition. Error bars and the shaded bands in (A) and (B) represent the 99% CI with $N = 36$. The colored solid lines are interpolation curves provided as a guide to the eye and were constructed directly from the raw discrete data points (dots). (C) Wavelength-dependent photocurrent acquired with lock-in. A negligible error of ± 0.0304 pA is measured at the baseline with $N = 50$. Middle inset shows the expanded view between 5170 and 5550 cm^{-1} . Wavelength ranges in which the molecule readily hopped in-plane are marked in dark gray. (D) IR-modulated tunneling current map at the $2\nu(\text{C-H})$ overtone (5934 cm^{-1}). (E) Photocurrent map acquired at 6060 cm^{-1} (off resonance). (F) Constant current STM topography acquired simultaneously with (D).

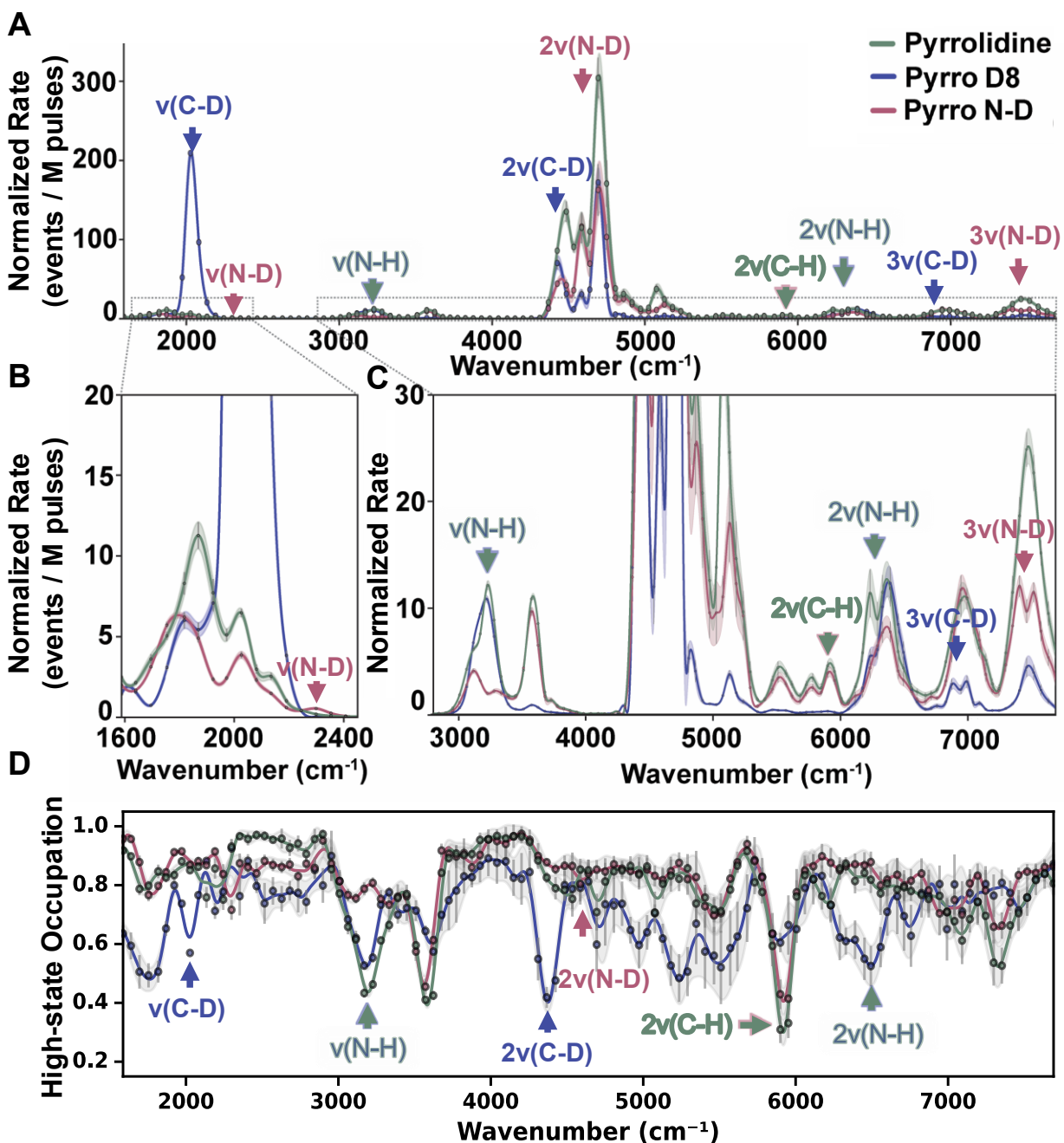


Fig. 4. Vibrational spectra of pyrrolidine and its deuterated isotopologues. (A) Comparison between pyrrolidine (green), Pyrro D8 (blue), and Pyrro N-D (red) showing the switch rate as a function of wavenumber. The fingerprinting vibrations of each isotopologue are labelled with arrows. (B) Expanded view between 1600 and 2400 cm^{-1} highlighting $v(\text{C-D})$ and $v(\text{N-D})$. (C) Expanded view between 2800 and 7600 cm^{-1} highlighting higher-order vibrational modes. The energy splitting observed at $3v(\text{C-D})$ and $3v(\text{N-D})$ are attributed to Fermi resonance. (D) Comparison of the “High” state occupation ratio of three isotopologues. The error bars and the shaded bands in all panels represent the 99% CI with $N = 36$. Colored solid lines are interpolation curves provided as a guide to the eye and were constructed directly from the raw discrete data points (grey dots).

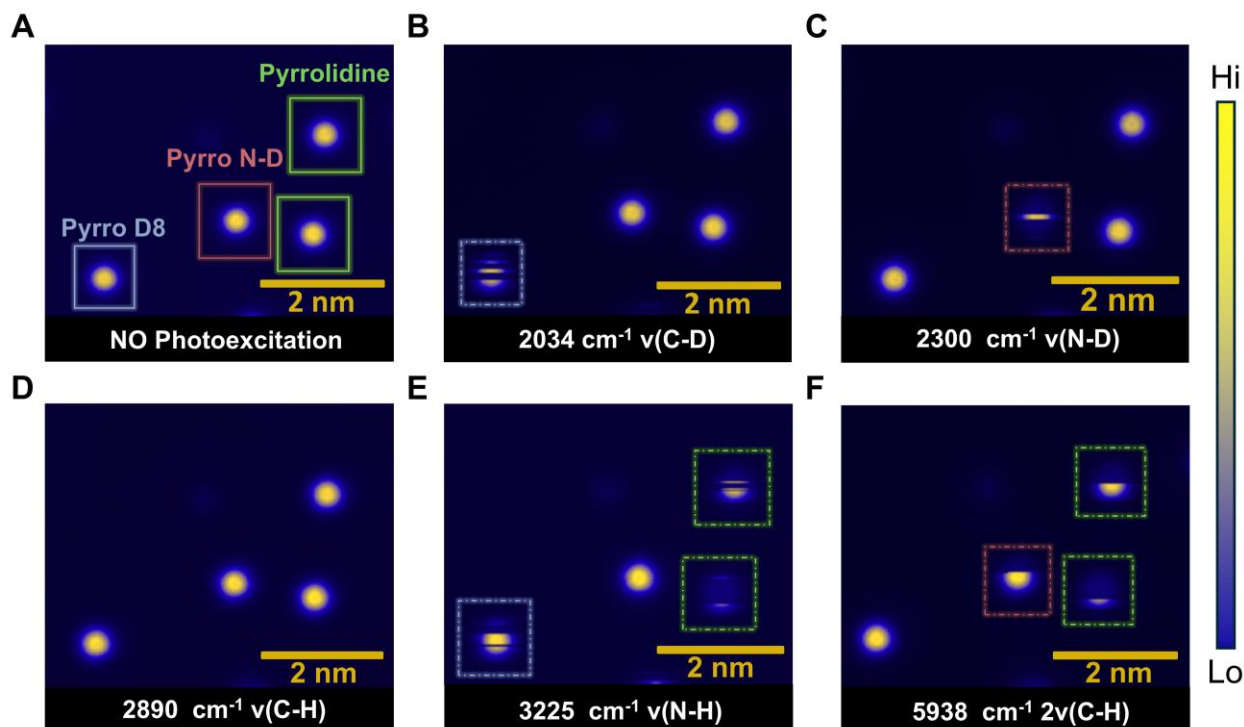


Fig. 5. Microscopic visualization of isotope-specific IR excitation in pyrrolidine and its deuterated isotopologues. (A) Constant-height STM images acquired without IR excitation, showing morphologically identical pyrrolidine (green boxes), Pyrro N-D (red box), and Pyrro D8 (blue box) molecules. (B-F) Selective vibrational excitation at different frequencies: (B) $\nu(\text{C-D})$ of Pyrro D8 (2034 cm^{-1}); (C) $\nu(\text{N-D})$ of Pyrro N-D (2300 cm^{-1}); (D) $\nu(\text{C-H})$, showing no detectable response (2890 cm^{-1}); (E) $\nu(\text{N-H})$ of pyrrolidine and Pyrro D8 (3225 cm^{-1}); and (F) $2\nu(\text{C-H})$ of pyrrolidine and Pyrro N-D (5938 cm^{-1}). Colored dashed boxes highlight molecules exhibiting vibration-mediated switching at the corresponding excitation frequencies. Imaging conditions: $V_b = 20\text{ mV}$. The color scale represents the tunneling current from low (blue, 20 pA) to high (yellow, 800 pA)

Supplementary Materials include:

Materials and Methods

Supplementary Text

Supplementary Figs. S1 to S18

Tables S1 to S5

References (42, 53-64)



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Supplementary Materials for
Single-Molecule Infrared Spectroscopy with Scanning Tunneling Microscopy

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Materials and Methods
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1. Materials and Methods

1.1. Sample and Tip Preparation

Scanning tunneling microscopy (STM) and infrared integrated STM (IRiSTM) measurements were performed using a customized CreaTec ultrahigh-vacuum (UHV) STM operating at ~6-8 K (temperature with laser illumination) or 5.3 K (base temperature with optical access blocked) with a base pressure below 1×10^{-10} Torr. The STM cryostat was connected to a home-built helium recovery system to allow for continuous operation near its base temperature (53). Tungsten (W) tips were prepared by electrochemical etching (54). Both the Cu(100) single-crystal substrate and the W tips underwent at least three cycles of Ar⁺ sputtering (1.0 keV, 6 mA, 15 min) followed by thermal annealing (55). Surface cleanliness was verified by STM imaging, confirming atomically flat terraces free from contaminants. Tip apexes were further conditioned by gentle controlled contact with the clean Cu(100) surface until single-molecule resolution and stable tunneling conditions were achieved.

Two acetylene isotopologues, C₂H₂ (Air Gas, 99.8%+) and C₂D₂ (CDN Isotopes, 99%), were used as precursors to generate the corresponding ethynyl radicals. Three pyrrolidine isotopologues were employed: pyrrolidine (Transene Company Inc., 99.9%), pyrrolidine-2,2,3,3,4,4,5,5-d₈ (Pyrro D8; Sigma-Aldrich, 98 atom % D), and pyrrolidine-1-d (Pyrro N-D; synthesized in-house).

Pyrro N-D was synthesized by adapting a prior literature procedure (56): a 1:1 (v/v) mixture of CDCl₃ (Sigma-Aldrich, 99.8 atom % D) and CD₃OD (Sigma-Aldrich, 99.8 atom % D) were placed over activated 4 Å molecular sieves and stored under dry nitrogen for several hours before use. To an oven-dried 25 mL Schlenk flask was added 2.0 mL pyrrolidine (24.2 mmol) and 10.0 mL 1:1 CDCl₃/CD₃OD, and the mixture was stirred under nitrogen for 3 hours. The solvent was removed under dynamic vacuum (ca. 100-200 mTorr), then a fresh volume of CDCl₃/CD₃OD was added. This process was repeated three times. After final evaporation, Pyrro N-D was obtained as a clear liquid. The ¹H nuclear magnetic resonance (NMR) spectrum (Fig. S1) showed essentially complete disappearance of the N-H signal at 2.20-2.25 ppm (57), confirming efficient deuteration.

To further verify N-H deuteration, we compared the Fourier transform infrared (FTIR) spectrum of synthesized Pyrro N-D spin-coated as a thin film onto a copper sheet with that of non-deuterated pyrrolidine measured under identical conditions. The Pyrro N-D spectrum exhibited a characteristic N-D stretching mode at 2420 cm⁻¹, which was absent in non-deuterated pyrrolidine (Fig. S2). However, sample preparation under ambient conditions for FTIR measurement posed a challenge: the partial and H/D exchange with atmospheric moisture was highly probable due to the hygroscopic nature of Pyrro N-D. This contributed to the presence of the ν(N-H) signal at 3250 cm⁻¹ in the Pyrro N-D FTIR. Importantly, the specific sample used for STM characterization was prepared without ambient exposure and was thus expected to have a significantly higher deuteration purity. Furthermore, the bulk-level contamination did not affect single-molecule IRiSTM characterization, as the probed signal originated from the individual molecules locally in the STM junction. Nevertheless, the FTIR and NMR measurements independently confirmed sufficient Pyrro N-D in our sample.

All isotopologues, acetylenes (C₂H₂/C₂D₂) and pyrrolidines (non-deuterated pyrrolidine, Pyrro N-D, and Pyrro D8), were deposited in sequence using a variable leak valve connected to room-temperature molecular sources onto the same Cu(100) substrate at 5.3 K, to enable direct comparison under identical experimental conditions. Low molecular coverages were used to ensure spatially isolated single molecules suitable for independent spectroscopic characterization. Topographic images were acquired either in constant-current mode with feedback engaged, or in

constant-height mode with feedback disabled, for time-dependent measurements of tunneling current (I) or tip height (Z).

To generate C₂H and C₂D, we used STM-induced sequential dehydrogenation of acetylene on Cu(100) following the previously reported procedures by Lauhon *et al.* (35). Stepwise cleavage of the C–H (or C–D) bonds was achieved by positioning the tip over the center of the molecule and applying bias-voltage pulses. Reaction progress was monitored in real time through changes in tip height (ΔZ). Based on prior studies, the minimum voltages required were approximately 2.8 V (H) / 3.8 V (D) for converting C₂H₂/C₂D₂ $\rightarrow$ C₂H/C₂D, and 2.1 V (H) / 2.7 V (D) for converting C₂H/C₂D $\rightarrow$ C₂. Accordingly, we used 3.0 V (500 pA) for C₂H₂ and 4.5 V (50 pA) for C₂D₂ dissociations. For C₂H₂ dissociation (Fig. S3A), the C₂H₂ $\rightarrow$ C₂H step produced a small rise in ΔZ in constant current mode, followed by a pronounced drop upon C₂H $\rightarrow$ C₂. For the deuterated acetylene (Fig. S3B), two ΔZ drops were observed, consistent with previous characterizations.

1.2. IRiSTM Measurements of Switching Rates

Mid-infrared excitation was supplied by a Light Conversion CARBIDE laser (40 W, 1030 nm, 1 MHz maximum repetition rate, < 250 fs nominal pulse duration). This laser pumped an ORPHEUS OPA/DFG to generate tunable 1300–6300 nm pulses. The pulse duration corresponded to a transform-limited spectral full width at half maximum (FWHM) of ~ 60 cm⁻¹ which set the upper bound of the current IRiSTM spectral resolution. This resolution could be improved by using continuous wave rather than pulsed light. The p-polarized beam entered the UHV chamber at 60° incidence through a sapphire viewport and was focused onto the STM junction with an achromatic lens ($f = 15$ mm, $\varnothing = 12$ mm, Edmund Optics) rigidly mounted to the scanner, so the focal point co-moved with the tip. CCD profiling indicated a $1/e^2$ spot diameter of $\sim$ tens of μ m at the sample.

IRiSTM measurements of action rates were performed in the constant-current mode. For ethynyl (C₂H) radicals and its deuterated isotopologue (C₂D), measurements were conducted at 7.05 K with $V_{\text{bias}} = 30$ mV and $I = 20$ pA. At each excitation wavelength, the two neighboring species were probed sequentially, ensuring that all datasets at a given data point were acquired under identical conditions. The laser power was maintained at or below 6 mW to ensure thermal stability while resolving all vibrations that were able to couple with the in-plane rotation.

For pyrrolidine (C₄H₉N) molecules and its isotopologues (Pyrro N–D and Pyrro D8), experiments were performed at 6.29 K with $V_{\text{bias}} = 20$ mV and $I = 20$ pA. As above, sequential acquisition at each excitation wavelength ensured identical tip conditions across all isotopologues. The laser power was limited to ≤ 2 mW to prevent unnecessary thermal artifacts. Upon resonant IR irradiation, individual pyrrolidine molecules displayed telegraphic switching between “High” and “Low” conformers, which was observed as discrete ΔZ jumps of 0.65 ± 0.05 Å.

Wavelength-dependent absorption spectra were obtained by tuning the OPA across 1300–6300 nm. At each wavelength, the laser repetition rate was typically set to 1 MHz. The time required for 100 switching events was recorded 25–40 times. The unnormalized switch rate was calculated as $100 / \langle \text{time} \rangle$. The error bars were reported as the 99% confidence interval (CI, calculated as $\text{Mean} \pm t_{0.995, N-1} \times \text{Standard Error of the Mean}$). After each record the tip was automatically re-centered on the molecule using a home-built LabVIEW program to compensate for any lateral drift of the tip. All data were collected after the system had thermally stabilized at the target temperature ($\sim 6.29/7.05$ K) for > 1 h.

For wavelength ranges that yielded high switching rates beyond the STM time resolution, we first adjusted the laser power at the maximum 1 MHz repetition rate to keep the pulse energy at the junction constant, which was verified by the consistent STM temperature (additional discussion about temperature-power relation is presented in section 2.5). We then used a pulse picker to reduce the repetition rate until the switching rate stabilized at 4–5 events/s. The switching

rate was reported as the number of switching events per 1 M laser pulses. This strategy was justified because each laser pulse excited the molecule from its vibrational ground state as the vibrational lifetime (on the picosecond scale) was far shorter than the dwell time between adjacent laser pulses even at the maximum 1 MHz repetition rate. Meanwhile, spontaneous switching was negligible compared with the IR induced actions. Consequently, increasing the dwell time did not affect the underlying excitation dynamics. Vibrational modes identified as inactive were further tested by increasing the laser power by at least a factor of four; the absence of any response under these enhanced conditions confirmed that these modes did not mediate the observed action. Finally, we normalized the measured switching rates by applying a unitless scaling factor of $\lambda_{\text{ref}}/\lambda$ (with $\lambda_{\text{ref}} = 6300$ nm, the upper bound of the wavelength used in this study), yielding switching rates that corresponded to a constant photon flux to provide the absorption spectrum linearly correlated with the photo-excitation cross section (additional discussion is presented in section 2.5).

1.3. IRiSTM Measurements of IR-Modulated Tunneling Current with Active Z Compensation

To reliably detect light-induced photocurrents at the single-molecule level, we employed a lock-in detection scheme by modulating the laser with a mechanical chopper. Such modulation inevitably induced thermal expansion and contraction of the STM junction, which generated background signals that obscured the true photocurrent response. To address this issue, we implemented an active Z compensation scheme (28). The 1 MHz laser pulse train was chopped at a frequency below 400 Hz (f_{mod}) using a phase-locked mechanical chopper (Thorlabs MC2000B). The tunneling current was demodulated with a lock-in amplifier referenced to f_{mod} . In the absence of Z compensation, periodically chopped mid-IR illumination led to photoheating that synchronously expanded both the metallic tip and the sample, producing oscillations of the tip-sample separation and corresponding current modulation at f_{mod} (Figs. S4A and S4C) that were independent of the tip position. Fourier analysis revealed a pronounced peak at the chopping frequency (Fig. S4E).

To suppress this thermal background, we applied a counter-oscillation to the Z piezo. All photocurrent spectra and mapping were collected at $V_{\text{bias}} = 81$ mV and $I = 380$ pA, with tunneling feedback disabled and each data point averaged 15 times. Between scans at different infrared wavelengths, the Z compensation was adjusted and optimized. The tip was positioned over bare Cu(100) and the system was allowed to stabilize until negligible tip drift was observed (<0.1 Å over 5 min). The bias and current were then ramped to the measurement setpoints. After disabling the feedback loop, the thermally induced current oscillation was recorded. A Z-piezo drive at f_{mod} was subsequently enabled, and its amplitude and phase were swept until the lock-in signal at the f_{mod} was minimized to the noise floor (Fig. S4B, S4D, and S4F). Once thermal compensation was achieved, the tip was positioned over the target molecule, and the photocurrent spectra were acquired under fully stabilized conditions. This active compensation strategy ensured that thermal artifacts were rigorously suppressed, achieving a photocurrent resolution at the sub-picoampere scale (Figs. S4D and S4F). At baseline, the photocurrent exhibited random fluctuations of ± 0.0304 pA around a mean value of $I = 0.0426$ pA, reported with a 99% CI ($N = 50$).

1.4. STM Action Spectroscopy and Inelastic Electron Tunneling Spectroscopy

STM action spectroscopy was performed to probe vibrationally mediated switching via inelastic electron tunneling without IR excitation. Bias-dependent measurements were performed in constant-height mode. Current traces were acquired for 150 s ($V < 60$ mV), 90 s ($60 \text{ mV} \leq V < 90$ mV), or 60 s ($90 \text{ mV} \leq V \leq 120$ mV) to balance statistics with tip stability. The bias-dependent switching rate revealed vibrational thresholds corresponding to molecular modes accessible through electron-induced excitation.

The relation between transition yields and sample bias was calculated as $Y(V) = e/(\langle\tau\rangle \times I)$, where $\langle\tau\rangle$ is the average residence time and I is the tunneling current. Following the Ueba-Kim model (30), data were fitted to:

$$Y(V) = K_{\text{eff}} \frac{F(V, \hbar\Omega, \sigma_{\text{ph}})^n}{V}$$

where K_{eff} is an effective prefactor, $\hbar\Omega$ the vibrational energy, σ_{ph} is the broadening factor, and F is the dispersion function assuming Lorentzian vibrational density of states. The reaction order was fixed at $n = 1$, consistent with single-electron processes.

Inelastic electron tunneling spectroscopy (IETS) was obtained by lock-in detection of the second harmonic of the tunneling current (d^2I/dV^2) with 8 mV rms voltage modulation at 413 Hz, with feedback disabled at $V = 500$ mV and $I = 700$ pA, positioning the tip ~ 0.25 Å closer than in action spectroscopy to enhance the signal noise ratios. Spectra were averaged over 120 scans and processed using a three-point smoothing algorithm. All identified features were observed in both bias polarities, confirming their origin as molecular vibrations rather than spectral singularities.

1.5. Reflectance FTIR Spectroscopy

FTIR spectra were collected on a Bruker Tensor 37 spectrometer equipped with a liquid-nitrogen-cooled MCT detector and continuously purged with dry air from a purge gas generator to best suppress atmospheric H_2O and CO_2 ; reflection-mode data were recorded over the 1480–7000 cm^{-1} spectral range at 4 cm^{-1} resolution with 64 co-added scans. A background single-channel spectrum was first acquired from a clean Cu substrate, after which the same holder—now bearing either a pyrrolidine liquid thin film or a vapor-deposited adsorbate layer—was inserted without disturbing the optical alignment and measured under identical conditions. Raw spectra were processed in OPUS v7 by dividing the Cu reference, applying a concave rubber-band baseline correction (64 points, 15 iterations), vector-normalizing to the 2850–2950 cm^{-1} region, and exporting the results as 32-bit CSV files for further analysis.

1.6. NMR Spectroscopy

^1H NMR spectra were recorded on a 300 MHz Bruker AVA spectrometer at 298 K. Chemical shifts (δ) were reported in parts per million (ppm) using the residual solvent signals as the internal standard for proton and carbon spectra (Chloroform-*d*: δ_{H} 7.26 ppm).

1.7. Computational Modeling

Geometry optimization, vibrational mode analysis, and energy calculations were carried out using density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) with the projector augmented wave (PAW) method (58). The exchange-correlation energy was treated using the generalized gradient approximation (GGA) as formulated by Perdew-Burke-Ernzerhof. The Cu (100) substrate was modeled using a $4 \times 4 \times 1$ supercell with a thickness of four atomic layers. A vacuum of 20 Å was added along the z-axis to prevent spurious interactions with the neighboring images. A plane wave cutoff energy of 500 eV was used for all calculations. A Γ -centered Monkhorst-Pack k-point mesh was adopted for the Brillouin-zone integration.

The convergence criterion for the electronic self-consistent loop was set to 10^{-6} eV. All structures were relaxed until the Hellmann-Feynman forces on each atom were less than 10^{-3} eV/Å. The vibrational properties were calculated by the central-difference method with a displacement step of 0.015 Å. The climbing image nudged elastic band (CI-NEB) method was employed to locate the transition states (59). During the calculation, each image was relaxed until the force on each atom was less than 0.01 eV/Å. The van der Waals (vdW) interactions were evaluated by DFT-D3 method with the Becke-Johnson damping function (60) in all calculations.

2. Supplementary Text

2.1. FTIR Spectroscopy of Pyrrolidine

To provide reference data for the single-molecule IRiSTM spectra and validate our vibrational mode assignments, we performed FTIR spectroscopy on Cu surface-adsorbed pyrrolidine in two coverages: as sub-monolayer adsorbates and as a thin molecular film on Cu surfaces (Fig. S5). Spectra were normalized to the feature at approximately 2960 cm^{-1} (upper panel in Fig. S5) and 1450 cm^{-1} (bottom panel), respectively. The FTIR spectra exhibited characteristic fundamental vibrational modes of pyrrolidine below 3500 cm^{-1} . In the C–H stretching region ($2800\text{--}3000\text{ cm}^{-1}$), we observed the symmetric $\nu_s(\text{C–H})$ at 2875 cm^{-1} and asymmetric $\nu_{as}(\text{C–H})$ at 2960 cm^{-1} , consistent with literature values (46). The N–H stretch appeared at 3225 cm^{-1} in the thin film spectrum, while the CH_2 scissoring mode $\beta(\text{CH}_2)$ manifested at 1450 cm^{-1} . The sub-monolayer adsorbate spectrum showed narrower fundamental peaks due to the well-defined local potential of isolated molecules but noisier due to the reduced number of adsorbed molecules. The broader linewidth in the thin film bands was attributed to the hydrogen-bond-induced inhomogeneous broadening.

Notably, the N–H stretch at 3225 cm^{-1} appeared prominently in the thin film but fell below the noise floor in the sub-monolayer adsorbate spectrum despite using high-sensitivity MCT detector. For p-polarized IR radiation incident at 60° on a metallic surface, only vibrational modes with transition dipole moments perpendicular to the surface can couple to the electric field—parallel components experience destructive interference from image dipoles in the metal. Our DFT calculations confirmed pyrrolidine adsorbed through its nitrogen lone pair with the C–N–C plane nearly parallel to Cu(100), positioning the N–H bond almost parallel to the surface (tilt angle $<5^\circ$) (Fig. S9). This orientation rendered the N–H stretch IR-inactive in far-field FTIR. Conversely, the signal's emergence at thin-film coverage was the classic signature of IR intensity enhancement due to molecular aggregation resulting from the ordered intermolecular N–H $\cdots$ N hydrogen bonding. In IRiSTM, on the contrary, the near-field effect beneath the tip relaxes these selection rules (60), enabling detection of modes even with predominantly in-plane transition dipoles including the N–H stretch.

In the FTIR spectral region above 3500 cm^{-1} , weak overtone and combination bands appeared with dramatically reduced intensity. By expanding the vertical scale by factors of 5–10, features including $\beta(\text{CH}_2) + \nu_{as}(\text{C–H})$ near 4400 cm^{-1} , $2\nu(\text{C–H})$ at 5920 cm^{-1} , and $2\nu(\text{N–H})$ around 6250 cm^{-1} became visible. These bands were typically 100–1000 times weaker than fundamentals in FTIR due to anharmonicity requirements. In contrast, IRiSTM circumvents the weak optical cross sections that limit overtone detection through the coupling of vibrational excitation to conformational switching that amplifies the observable signal.

2.2. Comparison Between IRiSTM and STM-IETS/Action Spectroscopy of Pyrrolidine

IRiSTM offered distinctive, and more comprehensive insights when compared with STM based action spectroscopy (22) and IETS (21), two well-established techniques for vibrational characterization based on inelastic electron tunneling. For pyrrolidine, either STM action spectroscopy or IETS (Fig. S6) revealed only a subset of fundamental vibrational modes and was largely insensitive to the overtone and combination bands that were clearly observed by IRiSTM. Specifically, IETS (Fig. S6B) was intrinsically limited in detecting multi-quanta vibrational excitations, as these processes require higher-order electron–vibration couplings, which are inherently weak (61). In the meantime, the STM action spectroscopy (Figs. S6C, D) was dominant by the low-energy ($<120\text{ meV}$) ring modes that coupled most strongly to the switching reaction coordinate. Conformational switching became too fast to resolve at bias voltages above 120 mV ,

making information regarding the higher-energy vibrations inaccessible. Interestingly, although the fundamental $\nu(\text{C-H})$ mode appeared inactive in IRiSTM, it emerged as the strongest features in the IETS data. This contrast highlighted the distinct selection rules governing IRiSTM and IETS, which will be further discussed in section 2.4.

2.3. Bias-Dependent Action Spectroscopy of Pyrrolidine

To identify lower energy vibrational modes that directly coupled with the pyrrolidine structural transitions, we performed bias-dependent action spectroscopy of pyrrolidine and its isotopologues. Fig. S7 shows the normalized switching yields for both “High-to-Low” and “Low-to-High” transitions as a function of sample bias for pyrrolidine (Fig. S7A), Pyrro N-D (Fig. S7B), and Pyrro D8 (Fig. S7C). All measurements were acquired with feedback disabled at a tunnel junction set at 50 mV/20 pA.

The switching yield, defined as the normalized transition probability per electron, increased monotonically with bias voltage and displayed stepwise features at specific energies corresponding to vibrational modes. These thresholds were extracted by fitting the data with the Ueba–Kim model (refer to section 1.4). Each step marked the onset of a new inelastic excitation channel.

For pyrrolidine “High-to-Low” transitions, three thresholds corresponding to the “Low” state vibrations were observed at 45.57 meV [$\delta(\text{Cu-N})$], 78.84 meV [$\nu(\text{Cu-N})$] and 111.17 meV [$\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})$] (indicated by arrows in Fig. S7A). The “Low-to-High” branch shows two thresholds at 58.37 meV [$\delta(\text{Cu-N})$] and 76.60 meV [$\nu(\text{Cu-N})$]. DFT-calculated modes are given in Fig. S15.

Pyrro N-D displayed similar thresholds with minimal shifts, except the ~ 7 meV red-shift of the $\nu(\text{Cu-N})$ in the “High” state (71.66 meV vs. 78.84 meV), reflecting the change in the effective mass from isotopic substitution, as shown in Fig. S7B and Fig. S17.

Fully carbon deuterated Pyrro D8 showed more pronounced red-shifts in corresponding vibrational energies: “High-to-Low” thresholds at 60.84 meV [$\nu(\text{Cu-N})$], 77.00 meV [$\beta(\text{N-C}_2)$], 94.69 meV [$\omega(\text{CD}_2)$] and 119.45 meV [$\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})$] (Fig. S7C and Fig. S16). No clear stepwise features were detected for the “Low-to-High” transition above 60 mV, suggesting that the switching was predominantly driven by lower-energy vibrations below our measurement window.

2.4. Distinct Selection Rules in IRiSTM versus Inelastic Electron Tunneling

The bias-dependent action spectroscopy (Fig. S7) and IETS measurements (Fig. S6B) differ fundamentally from IRiSTM in characterizing pyrrolidine vibrations in two key ways. (i) IETS intensities scale with the electron–vibration coupling matrix element rather than with the infrared transition dipole. The localized C–H stretch is known to have a high excitation cross section by inelastic electron scattering. (ii) While the C–H mode can be excited by IR photons as confirmed through FTIR, its intrinsic vibrational motion is decoupled from the motion of the ring alone with the reaction coordinate of the pyrrolidine switching. These two fundamental differences likely underlie the absence of the C–H stretch in the IRiSTM and its presence in IETS. The quantitative analysis regarding the 2nd factor is presented in section 2.8.

Specifically, in the IETS experiment, the high tunnelling current pumped a non-equilibrium population into the C–H stretch; in the meantime, we hypothesize that the longitudinal electric field beneath the tip down-shifted a low-frequency ring mode by a few millielectronvolts, bringing its multi-quantum overtone into quasi-resonance with the C–H fundamental. This Stark-induced near-degeneracy could open an efficient anharmonic intramolecular vibrational redistribution (IVR) pathway (2, 62) that rapidly populated the ring mode with larger sudden vector projection (section 2.8) that can trigger switching rapidly. Moreover, when IETS signals were measured at

higher bias voltages, the tunneling current was larger, leading to a substantially increased residence time of the molecule in a charged state. Molecular charging could further mix the vibrational matrix elements of the C–H stretching mode with those of the ring modes, thereby opening IVR pathways that may ultimately trigger molecular switching. Additionally, because the excitation volume was highly local in IETS, C–H pumping was strongly suppressed in the “Low” geometry, so the imbalance in “High-to-Low” switching favored the “Low” conformer. Conversely, chemical locking of the N site (e.g. N-methylation) eliminated the conductance dip altogether by blocking the conformational pathway.

Taken together, these distinctions between IRiSTM and inelastic electron tunneling likely account for the observed differences in selection rules. However, since the mechanisms governing vibrational excitation by inelastic electron tunneling are not yet fully understood, further theoretical investigation beyond the scope of the present study remains necessary.

2.5. Power Dependence of IR-induced Molecular Actions

To characterize the power dependence of the IR-induced switching process, we measured the switching rate as a function of laser power at 1 MHz repetition rate. As it was impractical to directly measure the incident power in the STM junction with a power meter, we used the STM stage temperature (T_{STM}), measured with a DT-670 series silicon-diode temperature sensor (Lake Shore) mounted on top of the STM base plate as a proxy for the time-averaged absorbed power. The underlying principle of this measurement scheme is the same as that of commercial photothermal power sensors. At steady state, the absorbed optical power P_{abs} is balanced by thermal conduction to the cryostat bath. This is described by:

$$P_{\text{abs}} = G_{\text{th}}(T_{\text{STM}} - T_0)$$

where G_{th} is the effective thermal conductance of the system and T_0 is the base temperature, measured to be 6.254 K (with optical access windows open, but without laser illumination). The absorbed power is related to the incident laser power, P_{inc} , by the substrate's effective absorption efficiency, η , such that $P_{\text{abs}} = \eta P_{\text{inc}}$. Combining these gives a direct relationship between temperature and incident power:

$$T_{\text{STM}} = T_0 + \frac{\eta}{G_{\text{th}}} P_{\text{inc}}$$

This shows that the measured temperature is expected to be linearly proportional to the incident laser power. For a process driven by single-photon vibrational excitation, the switching rate, Γ , is proportional to the rate of photon absorption by the molecule. This is given by:

$$\Gamma = \sigma \Phi_{\text{ph}} = \sigma \frac{P_{\text{inc}}}{h\nu} = \frac{\sigma G_{\text{th}}}{\eta h\nu} (T_{\text{STM}} - T_0)$$

where σ is the molecular absorption cross-section, Φ_{ph} is the photon flux, and $h\nu$ is the photon energy. This predicts a linear relationship between the switching rate and T_{STM} . Fig. S8 shows the switching rate of pyrrolidine molecules as a function of T_{STM} under resonant excitation at $\nu(\text{N–H}) = 3225 \text{ cm}^{-1}$. The observed linear relationship confirms single-photon absorption and ruled out multiphoton processes or nonlinear thermal mechanisms.

Using T_{STM} as a power metric provided an effective method to maintain constant effective power at the junction during wavelength scanning experiments. Since the incident beam needs to pass through multiple windows in the UHV chamber, the final laser power at the STM junction could vary with wavelength. Monitoring and adjusting the incident power to maintain constant T_{STM} ensured that the power delivered to the junction was constant. This provided a stable baseline, simplifying the final normalization of the raw data to photon flux ($\Phi_{\text{ph}} \propto \frac{P_{\text{inc}}}{h\nu}$), needed to generate a spectrum intensity depends linearly on the absorption cross section.

2.6. Simulated Reaction Pathways of the C₂H Rotation and Pyrrolidine Isomerization

Both ethynyl and pyrrolidine adsorption on the Cu(100) surface are best described as chemisorption, as established in prior studies (35, 41, 42). In particular, the chemisorption of ethynyl on Cu leads to a substantial rehybridization of the carbon framework, resulting in a C=C bond rather than the C≡C triple bond characteristic of the gas phase (33, 34). Fig. S9 shows the DFT-optimized stable adsorption geometries of C₂H and pyrrolidine in both conformations. Fig. S10 presents the reaction pathway for C₂H in-plane rotation (Fig. S10A) and the “High-to-Low” transition of pyrrolidine (Fig. S10B) on Cu(100), as obtained from the climbing image nudged elastic band (CI-NEB) method (59). For C₂H, the conformations before and after a 90° rotation are symmetry-equivalent, and thus the initial and final states possess identical energies. The rotational barrier was calculated to be 48 meV. For pyrrolidine, the “Low” state potential minimum is 20 meV higher than that of the “High” state. The energy barrier of this double-well potential landscape was simulated to be 52 meV from the “High” state minimum. These energies did not account for zero-point vibrational energy. As shown by the reaction pathway in Fig. S10B, the conversion between the “High” and “Low” states of pyrrolidine proceeded via a ring-puckering intermediate, representing a ring-puckering-mediated pseudorotation (63).

It is noteworthy that, because molecular transitions could occur on a much faster timescale than complete IVR, only the vibrational modes sufficiently coupled to the reaction coordinate could trigger the reaction, known as mode specificity in chemical reaction. Compared to thermal excitation, photon excitation could prepare the molecule into a highly localized vibrational excited state (bright mode) and therefore exhibit stronger directionality. In molecules, the vibrational energy associated with a specific mode cannot be arbitrarily redistributed; the efficiency of IVR is governed by the anharmonicity of the potential energy surface. If a photo-excited vibrational mode is weakly coupled to the reaction coordinate of the transition, including C₂H rotation and pyrrolidine “High-to-Low” switching, it could decay through other channels instead of triggering molecular isomerization. As a result, even if vibrational energy exceeds the energy barrier, transition may not occur if the vibrational coupling with the reaction coordinate is weak.

Fig. S10 represents the static potential landscape (without accounting zero-point energy) of C₂H (Fig. S10A) and pyrrolidine (Fig. S10B) transitions. For modes that are strongly coupled to the transition coordinate, their vibrational zero-point energies may vary across different intermediate conformations along the reaction path, effectively reshaping the potential energy landscape. Consequently, even if the excitation energy is lower than the static barrier height shown in Fig. S9, switching may still be induced via this anharmonic coupling, which explains the observed switching at ~40 meV in Figs. S6C and S7.

Taken together, when strong anharmonicity exists, the energy-based criteria alone, i.e., whether the vibrational excitation energy exceeds the static barrier, are not sufficient to determine whether a given vibrational mode acquired through the zero-order harmonic approximation can induce the structural transition. Instead, the coupling strength between the vibrational mode and the reaction coordinate becomes the key determinant for evaluating the transition efficiency. This concept is adopted from the “Sudden Vector Projection” framework proposed for simpler molecules in previous studies (50). In the following analysis, we retain this terminology and provide a detailed examination of how this projection influences our experimental observations.

2.7. Anharmonic Overtone Activation and Vibrational Energy Flow

Building on the coupling-based criteria established above, we performed DFT normal-mode analysis, projecting the vibrational displacement vector (the “sudden vector”) onto the switching reaction coordinate of pyrrolidine. This analysis highlighted the vibrational modes with significant ring-puckering character. Due to their delocalized vibrational wavefunctions inducing

coherent nuclear displacements across the cyclic framework, the zero-point amplitudes ($\Delta x \sim \sqrt{\frac{\hbar}{2\sqrt{k\mu}}}$) of these vibrations significantly exceed those of localized stretches. Their displacement scales with $\sqrt{n + \frac{1}{2}}$, so high-quantum excitations act as efficient “lever arms” for pyrrolidine isomerization.

For pyrrolidine switching, we characterized the IVR processes into two limiting cases. For strongly coupled vibrations (e.g., nearly degenerate modes), we assumed that IVR among these modes was complete prior to the chemical process. In contrast, weak coupling between other vibrations occurred on a much slower timescale than the molecular transition. Based on this simplification, two distinct energy-flow channels were identified. (i) Below $\sim 6000 \text{ cm}^{-1}$, IR-active fundamentals funneled energy via rapid IVR into spectroscopically dark ring modes strongly coupled to the transition; the pronounced 4700 cm^{-1} peak (consistent with combination bands listed in Table S1: $4 \times [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$ at 4700 cm^{-1} , Fig. 3A) exemplifies this pathway. (ii) Above this energy, IVR was quenched through vibrational auto-detachment (64), and only direct resonant pumping of transition-active modes survived, although their cross sections decay roughly as $\frac{1}{(n!)^2} \left(\frac{\partial^n \mu}{\partial Q^n} \right)^2$.

Isotopic substitution provided additional validation of these two energy-flow mechanisms. The dramatic enhancement of $\nu(\text{C-D})$ switching efficiency in Pyrro D8 (observed at 2034 cm^{-1} in Table S2 and Fig. 4A) arose from fortuitous energy matching between the C–D fundamental and ring-mode overtones, creating fast and efficient IVR pathways that were absent for the higher-frequency C–H stretch. Similarly, the complex splitting patterns observed in high-order N–D overtones (e.g., the 7400 cm^{-1} $3\nu(\text{N-D})$ peak in Table S3 and Fig. 4C) reflected Fermi resonances with ring-breathing modes, demonstrating the sensitive dependence of vibrational coupling on precise energy matching.

2.8. Transition Probability Analysis Based on Sudden Vector Projection

We adopt the following notation to represent specific vibrationally excited states. The normal mode coordinates of the “High” state molecule are denoted as $Q_1, Q_2, \dots, Q_N$, where $N = 3 \times N_{\text{atom}}$ corresponds to the total number of degrees of freedom for the adsorbed molecule. The normal modes are indexed in order of increasing vibrational energy. The vibrationally excited states are labeled using occupation number representation, i.e.

$$|\{n\}\rangle = |n_1, n_2, \dots, n_N\rangle = |n_1\rangle_1 \otimes |n_2\rangle_2 \dots \otimes |n_N\rangle_N,$$

where $|n_i\rangle_i$ is the n_i th excited states of Q_i vibration. The ground state is

$$|\{0\}\rangle = |0\rangle_1 \otimes |0\rangle_2 \dots \otimes |0\rangle_N.$$

The transition probability of the $|\{n\}\rangle$ excited state of the initial molecular conformation is:

$$\pi \propto \sum_i |\langle F_i | H | \{n\} \rangle|^2 \delta(E_{\{n\}} - E_{L_i}),$$

where H is the effective Hamiltonian mediating the transition, and $|F_i\rangle$ denotes the states of the final conformation with energy E_{L_i} . We need to sum over $|F_i\rangle$ because the final conformation of transition is uncertain. The overlap matrix element $\langle F_i | H | \{n\} \rangle$ determines transition probability.

The root-mean-square (RMS) vibrational displacement of both the C₂H and pyrrolidine molecule is on the order of $0.05 \text{ \AA}$, whereas the characteristic length scale of the switching process is approximately $1.5 \text{ \AA}$ (C–C bond length). This disparity implies that matrix elements arising from the harmonic terms in the Hamiltonian are approximately zero due to negligible wavefunction overlap. Consequently, the overlap between vibrational wavefunctions must arise from

anharmonic contributions, which are predominantly localized near the reaction coordinate. Therefore, the magnitude of the matrix elements is governed primarily by the behavior of the wavefunctions in the vicinity of the reaction pathway within coordinate space. For similar reasons, although the exact spatial distribution of the $|F_i\rangle$ is difficult to characterize, at relatively low energies, it can be reasonably approximated as a delta function localized near the equilibrium position of the final conformation in coordinate space.

To estimate the overlap matrix elements, we focus on the reaction coordinate, denoted as r , where $r = 0$ corresponds to the initial conformation and $r = r_0$ to the final conformation. For a given vibrationally excited state $\{n\}$, the relevant quantity is the probability distribution along the reaction coordinate, $f(r)$. Considering that the characteristic length scale of the reaction coordinate is significantly larger than the RMS displacement of molecular vibrations, the asymptotic behavior of the vibrational wavefunction within the range of the anharmonic potential can be well approximated by a Gaussian function. Consequently, the distribution $f(r)$ can also be qualitatively described by a Gaussian profile:

$$f(r) \propto e^{-\frac{r^2}{2r_{\text{RMS}}^2}},$$

where r_{RMS} is the RMS of r . Typically, $r_0 \gg r_{\text{RMS}}$. Considering the locality of $|F_i\rangle$, there is

$$\pi \propto |f(r_0)|^2 \propto e^{-\frac{r_0^2}{r_{\text{RMS}}^2}}.$$

This implies that the probability of switching is positively correlated with the value of r_{RMS}^2/r_0^2 for a given vibrationally excited state. Since r_0 is a constant independent of vibrational modes, the switching probability is effectively determined by the extent of the wavefunction along the reaction coordinate r_{RMS}^2 :

$$r_{\text{RMS}}^2 = \langle \{n\} | r^2 | \{n\} \rangle.$$

Next, we evaluate RMS value along the reaction coordinate. Near the equilibrium structure, the reaction pathway can be approximated as a straight line. Under this linear approximation, we denote the unit vector along the direction of the reaction pathway as $\hat{\mathbf{R}}$. In fact, $\hat{\mathbf{R}}$ represents the reaction vector under the assumption that IVR is negligible on the short timescale of the transition, corresponding to the so-called ‘‘sudden vector’’. Thus, the reaction coordinate can be expressed as a linear combination of the normal mode coordinates.

$$r = \sum_i^N c_i Q_i,$$

where

$$c_i = \hat{\mathbf{R}} \cdot \hat{\mathbf{Q}}_i.$$

Therefore

$$\begin{aligned} r_{\text{RMS}}^2 &= \langle \{n\} | r^2 | \{n\} \rangle = \sum_{i,j}^N c_i c_j \langle \{n\} | Q_i Q_j | \{n\} \rangle \\ &= \sum_i^N \mathcal{P}_i^2 (2n_i + 1), \end{aligned}$$

where the sudden vector projection is

$$\mathcal{P}_i = \sqrt{\frac{\hbar}{2\mu_i\omega_i}} \hat{\mathbf{R}} \cdot \hat{\mathbf{Q}}_i = \hat{\mathbf{R}} \cdot \hat{\mathbf{Q}}_i \Delta x_i.$$

where μ_i and ω_i are the effective mass and the frequency of Q_i vibration, respectively. Δx_i is the

RMS displacement of the ground state of Q_i vibration.

The probability that a specific vibrational mode of the molecule induces switching is primarily determined by the sudden vector projection, $\mathcal{P}_i$, and the excitation order of the vibrational states. We refer to this approach as the *coupling-based criterion*, as it characterizes the extent of coupling between the vibrational mode and the reaction coordinate. This method is applicable to vibrational states of various excitation orders, including combination bands.

For isotopically substituted molecules, the effective vibrational masses are generally larger, which leads to a reduction in the sudden vector projection $\mathcal{P}$. As a result, the transition probability decreases, consistent with the trend predicted by the kinetic isotope effect model. This provides a mechanistic explanation for the experimentally observed decrease in switching rates from pyrrolidine to Pyrro D8 and further to Pyrro N-D in Fig. 4.

In addition to the sudden vector projection, the experimental switching rate is also influenced by the probability of photon absorption, which is proportional to the squared magnitude of the transition dipole moment of a given vibrational mode. Figs. S14-S17 present snapshots of vibrational modes in C₂H, C₂D, pyrrolidine, Pyrro D8, and Pyrro N-D molecules that exhibit either significant sudden vector projection or large transition dipole moments. These vibrational modes correspond to those employed in the experimental peak assignments presented in Tables S1-S5. For each mode, the first-order transition dipole moment (p), the component perpendicular to the metal surface (p_z), and the sudden vector projection ($\mathcal{P}$) are labeled. The reaction-coordinate projection $\mathcal{P}$ is normalized such that the mode with the largest $\mathcal{P}$ is assigned to a value of 1.

2.9. Tip-to-Tip Variation in IRiSTM

While ideally all measurements would be acquired under identical tip conditions, tip changes inevitably occur during any STM measurements. In STM-TERS, the signal intensity is extremely sensitive to the condition of the tip, which constitutes a major experimental challenge (16, 19, 20, 23). However, because the spatial resolution of IRiSTM does not rely on field enhancement at the tip apex, we expect the tip to be less critical. To test this hypothesis, we compared IR-induced switching rates measured using three independently prepared STM tips. Each tip was conditioned by repeated indentation into the Cu(100) substrate through multiple cycles. This process closely mimicked the typical experimental procedures involved in STM tip preparation. The frequency-dependent response in the N-H stretching region exhibited consistent spectral profiles across all three measurements, with both amplitudes and peak positions indistinguishable within experimental error (Fig. S11A). Figs. S11B-D show the switching rates recorded with each tip at 3205 cm⁻¹. Each data point was averaged from 60 s of ΔZ time trace. The extracted switching rates remained statistically constant across all three tips, displaying only minor, uncorrelated fluctuations. These results demonstrated excellent tip-to-tip reproducibility in IRiSTM measurements, confirming that the observed spectral features reflected intrinsic molecular properties rather than tip geometry.

2.10. Fast Isotope Identification in Large Area Scans

As described in the Fig. 4, tuning the IR wavelength into resonance with specific X-H or X-D stretches (X = N or C) allowed microscopic discrimination of isotopologues. To statistically validate this observation, we include large-area scans encompassing more than 30 co-deposited molecules, as shown in Fig. S12.

Under resonant excitation of the C-D stretching mode, only Pyrro D8 exhibited characteristic stripe-like features (Fig. S12A). Subsequently, the laser was tuned to the N-D stretching frequency. Since Pyrro N-D possesses an intrinsic switching rate approximately four times higher than that of regular pyrrolidine, we optimized the laser pulse density to a near-

threshold level. In this regime, the excitation probability of non-deuterated pyrrolidine was negligible. Notably, this reduced photon flux also lowered the effective switching rate of the Pyrro N–D. To better distinguish the isotopologues, a smaller area was scanned to significantly increase the dwell time at each pixel (Fig. S12B). Furthermore, we imaged the same region under the first C–H overtone excitation, which activated both C–H-containing species—pyrrolidine and Pyrro N–D (Fig. S12C). By cross-referencing Figs. S12B and S12C, molecules that remained still under N–D excitation but became active under C–H overtone excitation were identified as non-deuterated pyrrolidine.

Following this microscopic identification, we parked the STM tip over individual molecules of interest and recorded their switching dynamics to further confirm the isotopologue assignment. Typical ΔZ versus time traces for each species are shown in Figs. S12D–F, exhibiting distinct switching behaviors characteristic of pyrrolidine (green), Pyrro N–D (red), and Pyrro D8 (blue) under their representative resonant vibrational excitations. These single-molecule measurements provided additional confirmation of the isotope-selective activation observed in the large-area topography, enabling unambiguous chemical identification at the single-molecule level.

2.11. Intactness of N–H of Pyrrolidine on Cu(100)

Dehydrogenation of N–H could spontaneously happen for some metal adsorbed molecules. Though such reaction was unlikely on Cu due to its inertness, we performed a controlled, stepwise dissociation on a single pyrrolidine, supported with DFT simulation, to validate the intactness of the N–H bond in surface adsorbed pyrrolidine. As shown in Fig. S13A, the ΔZ trace recorded at $V_{\text{bias}} = 2.3$ V and $I = 50$ pA exhibited two discrete steps that marked sequential dehydrogenation of the molecule. We assigned the first step ($\text{C}_4\text{H}_9\text{N} \rightarrow \text{C}_4\text{H}_8\text{N}$) to selective N–H bond scission, which was supported by DFT simulations, followed by further dehydrogenation of a C–H. STM images taken after each step (insets in Fig. S13A) showed distinct topographic signatures for these three states.

The N-dehydrogenated intermediate $\text{C}_4\text{H}_8\text{N}$ displayed bistability on the surface without rotation. High-resolution images (Figs. S13B–D) captured the molecule flipping between two equivalent geometries, referred to as “Top” and “Bottom” states. This topography agreed well with the DFT simulation of the N-dehydrogenated product (Fig. S13E): the optimized adsorption geometry placed the radical N atom at a bridge site following N–H cleavage, consistent with the experimentally observed two-state switching behavior. In contrast, the further C-dehydrogenated product exhibited no such switching behavior.

We further probed the vibrational activity of the intermediate product by STM action spectroscopy. The bias-dependent action spectroscopy for $\text{C}_4\text{H}_8\text{N}$ (Fig. S13F) exhibited a clear threshold at 367 mV in agreement with excitation of C–H stretching modes. No energy threshold corresponding to N–H vibration was observed, further supporting our conclusion of the selective N–H bond scission by electron pulse. Collectively, these observations confirmed that the N–H bond was intact in pyrrolidine upon surface adsorption.

2.12. “High” State Occupation Analysis for Pyrrolidine

In Fig. 4D, clear valley-like reduction in the “High” state occupation were observed when the vibrational modes $\nu(\text{C–D})$, $2\nu(\text{C–D})$, $3\nu(\text{C–D})$ and $2\nu(\text{C–H})$ were excited, indicating that the molecule tended to remain in the “Low” state under these resonances. As shown in Figs. S15–S17, the transition dipole moments of the C–H/C–D stretching modes in the “High” state pyrrolidine molecules were larger than those in the “Low” state, while their reaction-coordinate projections were nearly identical. This implies that “High” state molecules were generally more efficient at absorbing photons resonant with C–H/C–D stretch modes and switching to the “Low” state.

Similarly, valleys in the “High” state occupation spectrum were also observed near the $\nu(\text{N-H})$, $2\nu(\text{N-H})$ modes. Figs. S15 and S16 show that the N-H stretch modes in the “High” state possessed larger reaction-coordinate projections than in the “Low” state, whereas the corresponding transition dipoles were nearly the same. This explains why the excitation of the N-H stretch led to an increased preference for the “Low” state. Notably, no significant decrease was observed in the “High” state occupation at $\nu(\text{N-D})$, $2\nu(\text{N-D})$. Fig. S17 reveals that both the transition dipole moment and reaction-coordinate projection of the N-D stretch were comparable between “High” and “Low” states. Since the “High” state is energetically lower, the molecule showed a tendency to remain in the “High” state under N-D excitation.

Certain ring modes also contributed to valleys in the “High” state occupation spectrum. Around 1800 cm^{-1} , pyrrolidine and Pyrro N-D preferentially remained in the “High” state, whereas Pyrro D8 tended to favor the “Low” state (Fig. 4D). At this energy range, the switching was primarily driven by the mode $[\nu(\text{C}-\text{C})_{\text{para}} + \gamma(\text{N}-\text{H})]$. According to Figs. S15–S17, this mode exhibited comparable transition dipole moments between “High” and “Low” states for pyrrolidine and Pyrro N-D, while Pyrro D8 showed a significantly stronger transition dipole in the “High” state, explaining the observed tendency toward the “Low” state.

In the vicinity of 3600 cm^{-1} , pyrrolidine and Pyrro N-D again showed an increased preference for the “Low” state. In this region, switching was dominated by the mode $[\omega(\text{N}-\text{C}_2) + \gamma(\text{N}-\text{H})]$. Figs. S15 and S17 show that this mode had similar transition dipole strengths in both states, but significantly larger reaction-coordinate projections in the “High” state, resulting in a net preference for the “Low” state.

In the $5000\text{--}5500\text{ cm}^{-1}$ range, Pyrro D8 showed a much lower “High” state occupation compared to the other two molecules. This is because the measured modes in this region for Pyrro D8 were primarily combination bands composed of ring modes and $2\nu(\text{C-D})$, where the C-D stretch component favored switching to the “Low” state. Consequently, the “High” state occupation of Pyrro D8 was reduced in this spectral region.

2.13. Polarization Dependence of the “High” State Occupation

As discussed above, the “High” state occupation ratio depended sensitively on the imbalance between the “High-to-Low” and “Low-to-High” transition cross sections. Accordingly, maximal alignment of the electric field with the molecular dipole in the “High” conformation is expected to reduce occupation ratio in this state. Consequently, the polarization dependence of the “High” state occupation ratio could provide insights on the corresponding dipole orientations.

In polarization-dependent measurements at the $2\nu(\text{C-H})$ mode (Fig. S18), the “High” state occupation exhibited a minimum near $\sim 55^\circ/305^\circ$ (with 0° defined as p-polarized light aligned with the tip Z axis), consistent with the tilted orientation of the C-H bond relative to Z. In contrast, the occupation maximized near $0^\circ \pm 5^\circ$, corresponding to the C-H orientation in the “Low” state. This behavior supports our hypothesis that at $0^\circ \pm 5^\circ$ the “Low-to-High” transition is enhanced due to an increased IR absorption cross section, leading to a higher “High” state occupation, whereas at $\sim 55^\circ/305^\circ$ the “High-to-Low” transition dominates, minimizing the “High” state population. We note that the polarization dependence may also be influenced by STM tip geometry through tip-enhancement/screening effects, potentially contributing to the observed asymmetry in Fig. S18. Measurements of the occupation ratio at additional vibrational frequencies are expected to provide further insight into the dipole moments of the corresponding modes.

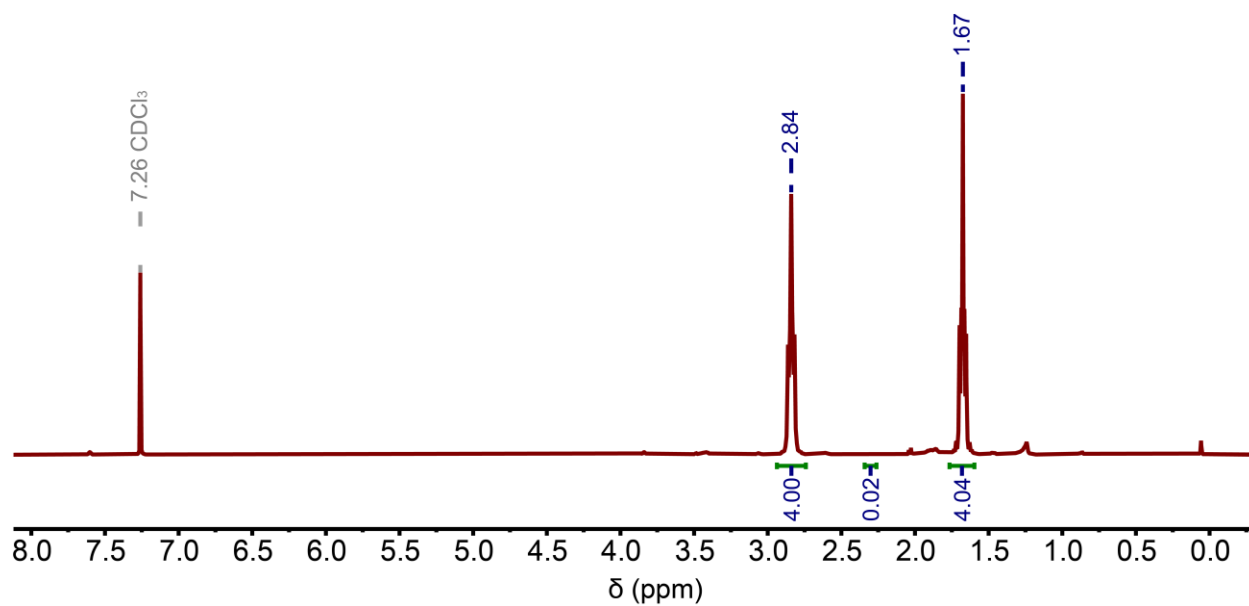


Fig. S1. ^1H NMR spectrum of Pyrro N-D. The N–H resonance at δ 2.20–2.25 ppm present in non-deuterated pyrrolidine is absent, confirming efficient deuteration at nitrogen. Remaining signals are ring methylene protons at δ 2.84 ppm (br s, 4 H, N–CH₂) and δ 1.67 ppm (br s, 4 H, CH₂), the residual proton signal in CDCl₃ appears at δ 7.26 ppm.

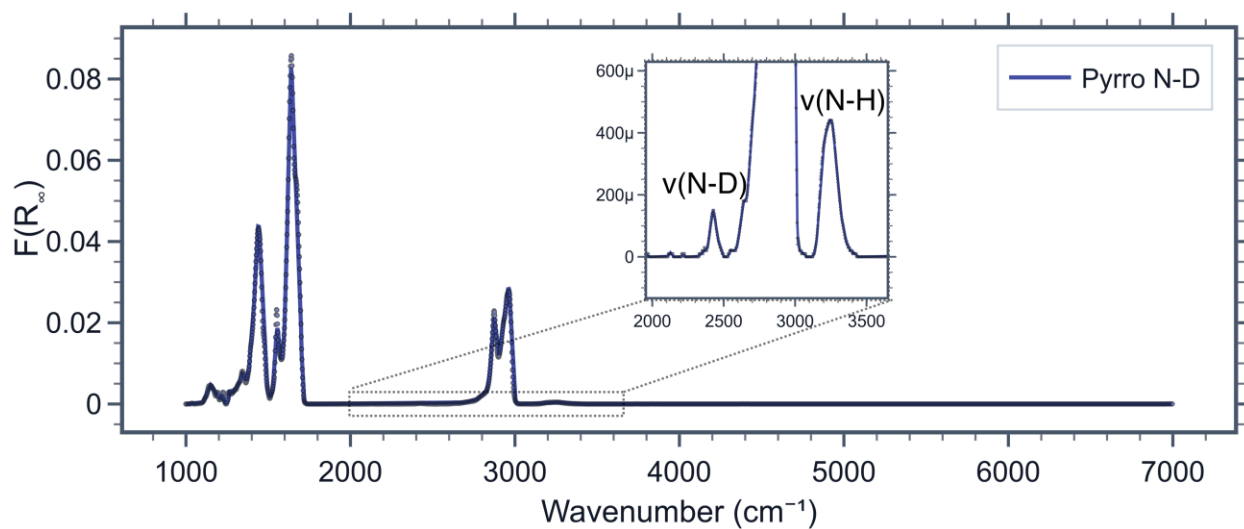


Fig. S2. FTIR spectrum of Pyrro N-D. A 2 μL aliquot was spin-coated to form a thin film; data are shown as the Kubelka–Munk-transformed reflectance $F(R_\infty)$ after baseline correction. The inset shows the wavenumber region (2000–3600 cm^{-1}), illustrating the N–D stretch at $\sim 2420 \text{ cm}^{-1}$, confirming the existence of Pyrro N–D. The N–H stretch at $\sim 3250 \text{ cm}^{-1}$ indicates non-deuterated pyrrolidine remains in the sample, which could either be due to the inefficient reaction or the partial H/D exchange occurring in the ambient conditions. Nonetheless, the non-deuterated pyrrolidine residues do not affect the IRiSTM measurement.

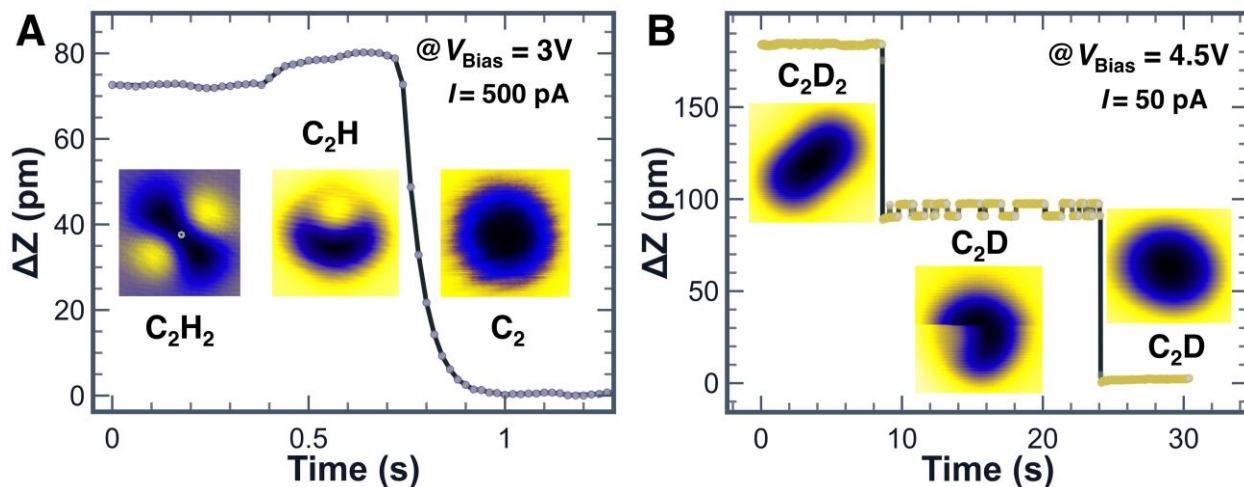


Fig. S3. Electron-induced sequential dehydrogenation of C_2H_2/C_2D_2 to ethynyl and C_2 on Cu(100). (A) Tip height change (ΔZ) versus time trace recorded over a C_2H_2 molecule during its stepwise dissociation into ethynyl (C_2H) and dicarbon (C_2) at 3.0 V and 500 pA. The process ($C_2H_2 \rightarrow C_2H \rightarrow C_2$) is characterized by a discrete increase in ΔZ followed by another decrease. (B) Analogous dissociation trajectory for deuterated acetylene ($C_2D_2 \rightarrow C_2D \rightarrow C_2$) recorded at 4.5 V and 50 pA. In this case, each dehydrogenation step resulted in a discrete drop in ΔZ . The insets display constant-current images corresponding to each identified molecular species. The black asterisk in (A) marks the tip position to induce this multi-step dissociation.

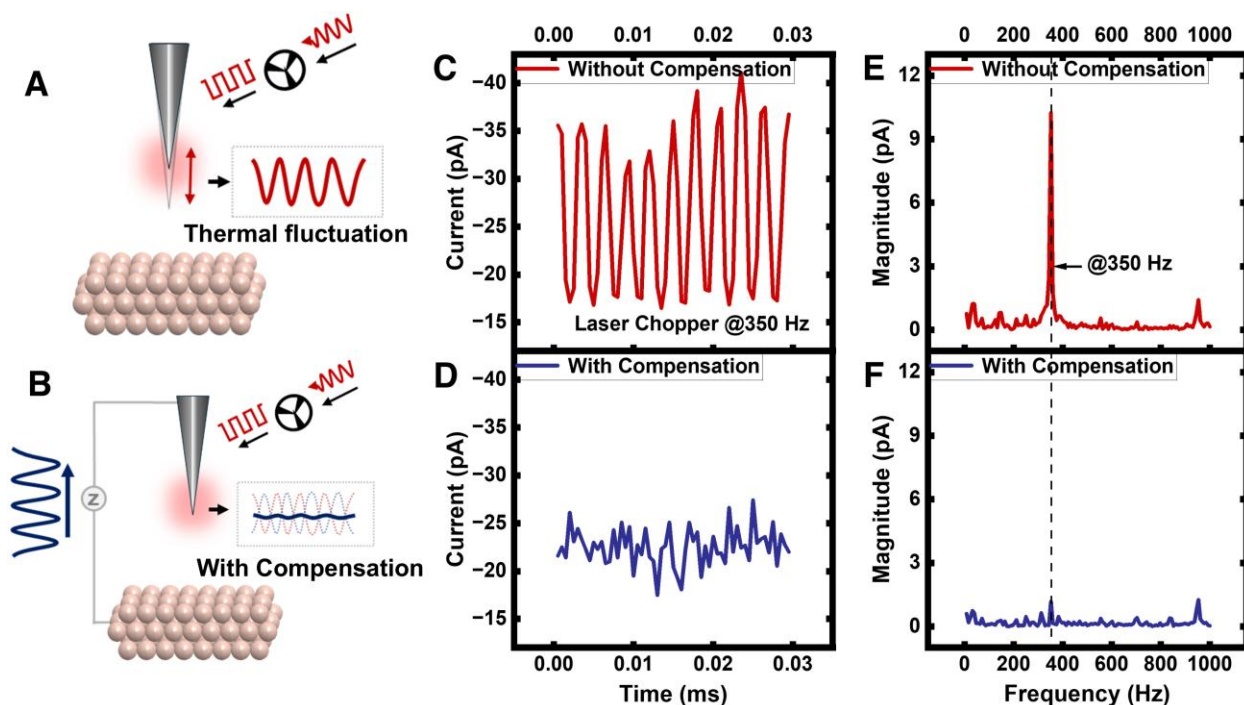


Fig. S4. Active Z compensation scheme to measure IR-modulated tunneling current of pyrrolidine on Cu(100). (A-B) Schematic of the thermal-compensation strategy. The laser intensity was modulated with a chopper (A), while the tip-sample distance Z was synchronously adjusted (B). By tuning the phase and amplitude of the Z modulation, thermal expansion was compensated, thereby minimizing oscillations in tip-sample distances. (C-D) Photocurrent trace recorded before (C) and after (D) implementing synchronous Z compensation. (E-F) Fast Fourier transform spectra of photocurrent traces recorded before (E) and after (F) applying Z compensation.

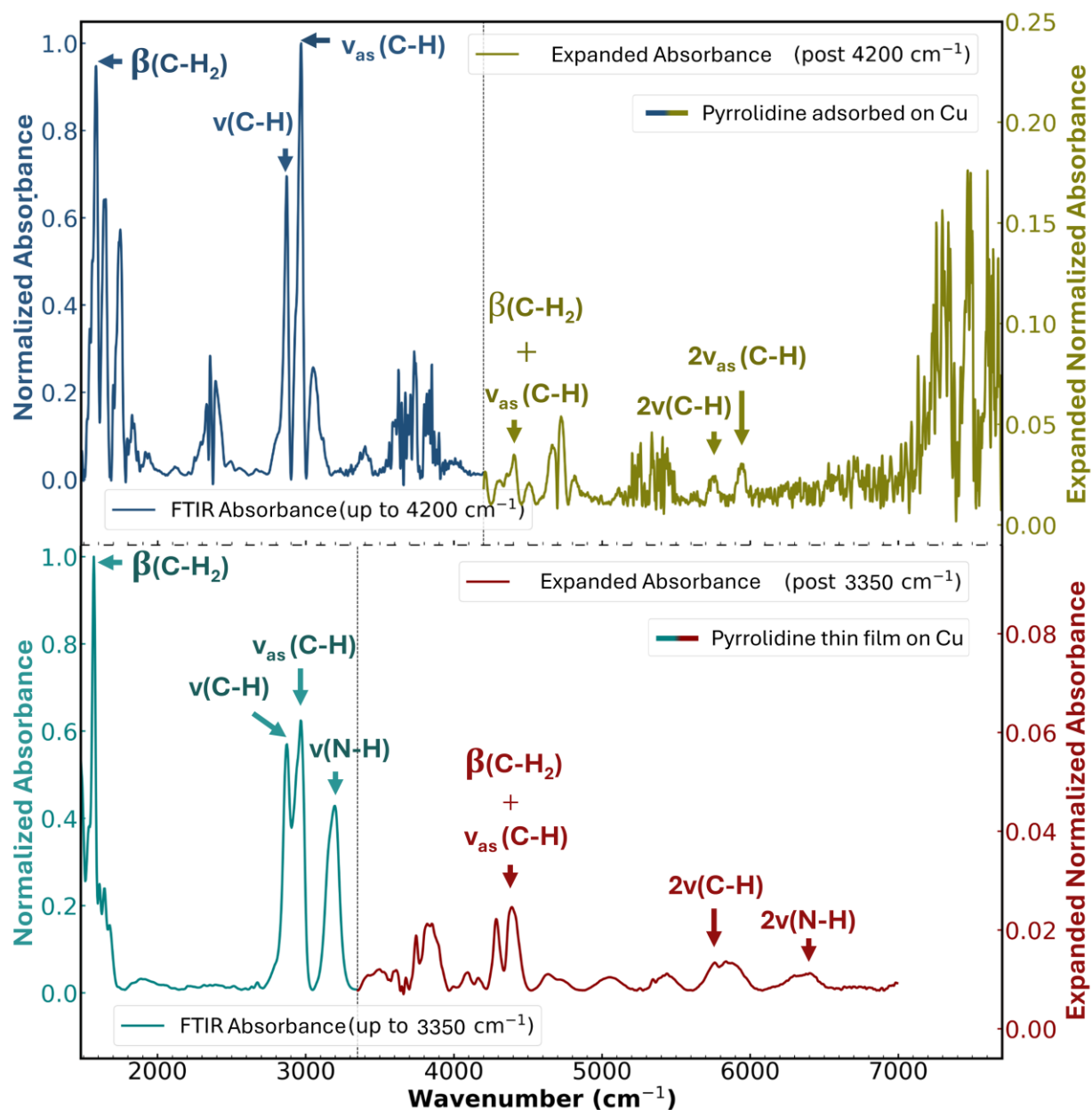


Fig. S5. Ensemble-averaged FTIR absorption spectra of pyrrolidine on Cu surfaces.

(Top) FTIR spectrum of sub-monolayer pyrrolidine adsorbates on Cu showing normalized absorption (blue, left axis) and expanded absorbance scale above 4200 cm⁻¹ (green, right axis). (Bottom) FTIR spectrum of pyrrolidine thin film on Cu showing normalized absorption (cyan, left axis) and expanded absorption above 3500 cm⁻¹ (red, right axis). Major vibrational modes are labeled, including fundamental C-H and N-H stretches, CH₂ scissoring (β), and overtone/combination bands. The N-H stretch at 3200 cm⁻¹ was present in the thin-film spectrum but absent for the adsorbate because its transition dipole lies parallel to the metal surface and was therefore suppressed by the surface-selection rule.

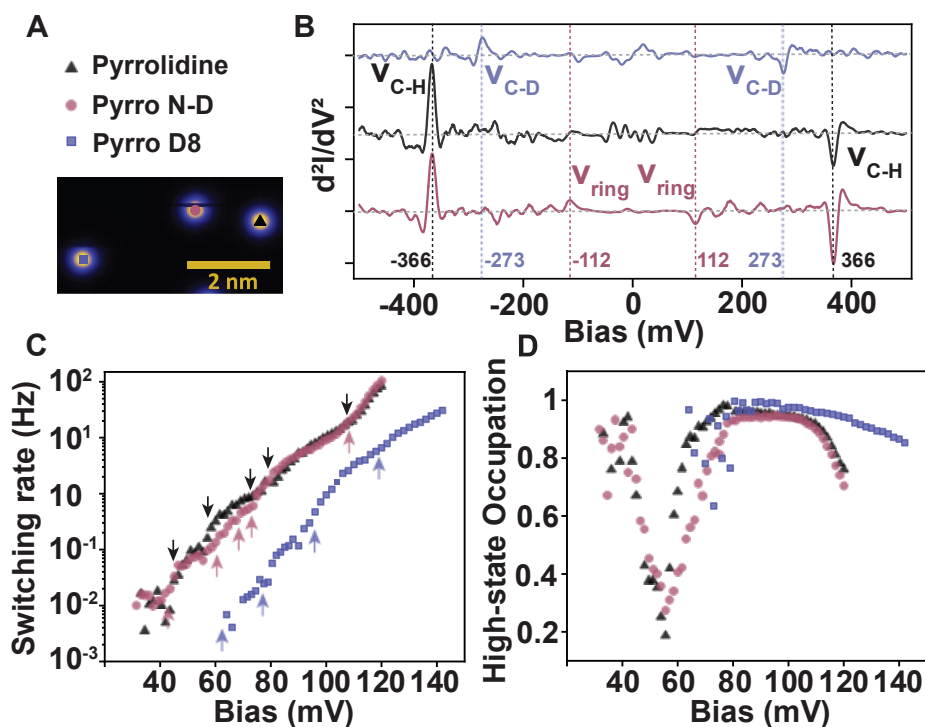


Fig. S6. Pyrrolidine conformational switching induced by inelastic electron scattering. (A) Constant-current STM image of nearby pyrrolidine (black triangle), Pyrro N-D (pink circle), and Pyrro D8 (blue square) molecules. (B) IETS (d^2I/dV^2) spectra of pyrrolidine (black), Pyrro N-D (red), and Pyrro D8 (blue), offset for clarity. Characteristic vibrational modes are labeled: $\nu(\text{C-H})$ at ± 366 mV, $\nu(\text{C-D})$ at ± 273 mV, and ring breathing at ± 112 mV. (C) Bias-dependent action spectroscopy showing switching rate (Hz) versus bias voltage (mV) on a semi-logarithmic scale. Arrows indicate step-like change in the switching rate corresponding to different vibrational thresholds. The small energy downshift in Pyrro N-D stemmed from N-metal out-of-plane bending, while the much larger shift in Pyrro D8 was due to the much heavier molecular mass. (D) Occupation ratio of “High” state as a function of bias (mV), revealing the negligible influence from substituting N-H with N-D but distinctive effects from substituting C-H with C-D.

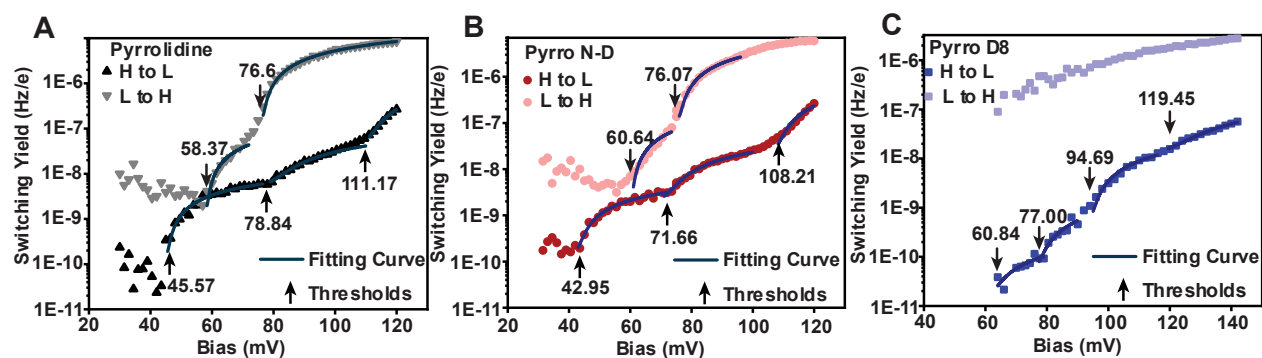


Fig. S7. Normalized “High-to-Low” and “Low-to-High” transitions yield as a function of bias voltage for (A) pyrrolidine, (B) Pyrro N-D, and (C) Pyrro D8. Black lines were fitted with the Ueba-Kim model. Arrows indicate vibrational thresholds extracted from the fittings. All data were acquired with feedback off at a tunnel junction set point of 50 mV and 20 pA. The systematic shifts in threshold energies with isotopic substitution confirmed the vibrational origin of the electron-induced switching process.

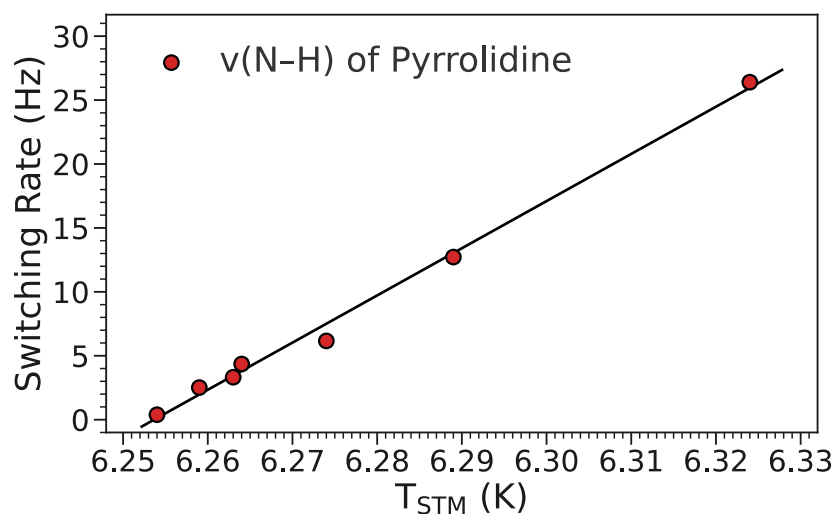


Fig. S8. Power dependence of pyrrolidine switching rate. Switching rate of pyrrolidine molecules as a function of STM stage temperature (T_{STM}) for resonant IR excitation at $\nu(\text{N-H})$ (3225 cm^{-1}), measured at 20 mV sample bias with feedback on at set point 20 pA. Since T_{STM} was proportional to the incident laser power, this plot represented the power dependence of the switching process. The black line is the linear fit to the data. This linear relationship confirmed single-photon resonant excitation, consistent with the expected behavior for vibrationally mediated switching at this wavelength.

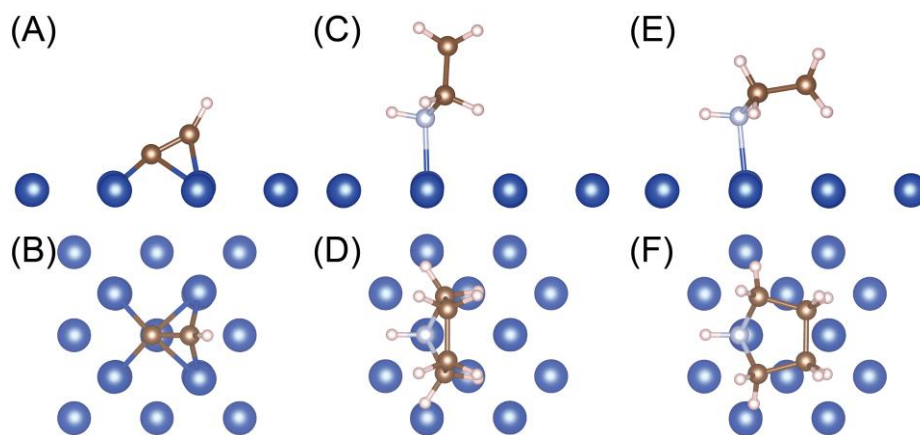


Fig. S9. DFT-optimized stable adsorption geometries of the molecules. (A-B) Simulated side (A) and top (B) views of C₂H adsorption on Cu(100). (C-F) Simulated side (C, E) and top (D-F) of pyrrolidine in the “High” (C-D) and “Low” (E-F) conformations.

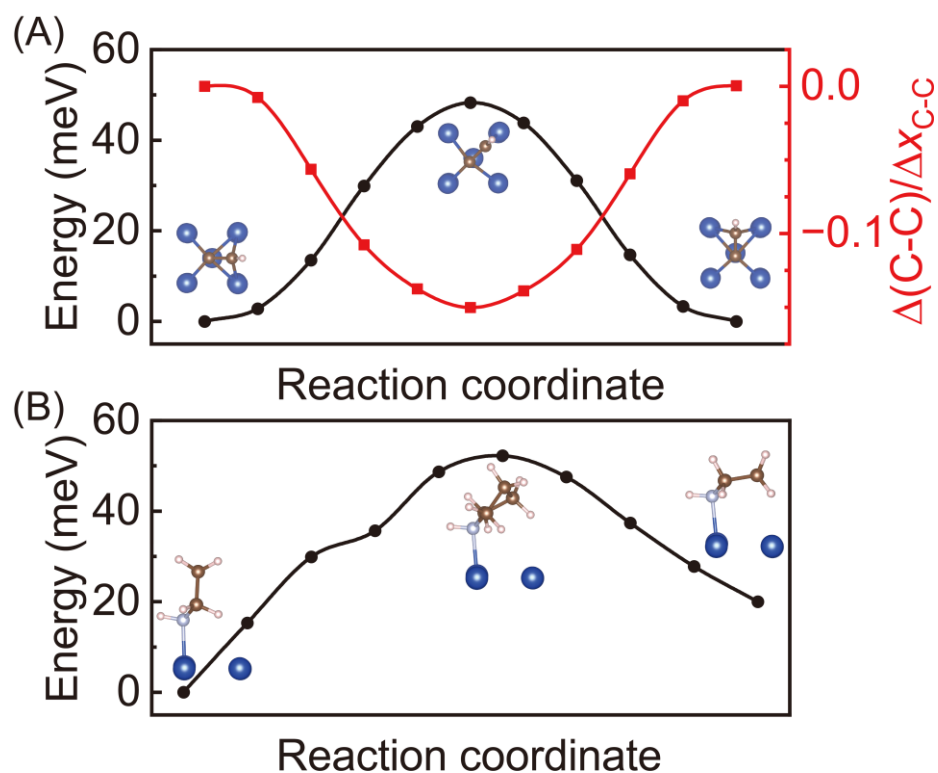


Fig. S10. Transition paths and the reaction barriers of (A) C₂H rotation and (B) pyrrolidine "High-to-Low" switching. Inset: the initial, transition, and final conformations of (A) C₂H rotation and (B) pyrrolidine "High-to-Low" switching. The red curve in panel (A) shows the change in the C=C bond length ($\Delta C - C$) of C₂H during rotation, normalized by the root-mean-square displacement of $v(C=C)$ (Δx_{C-C}).

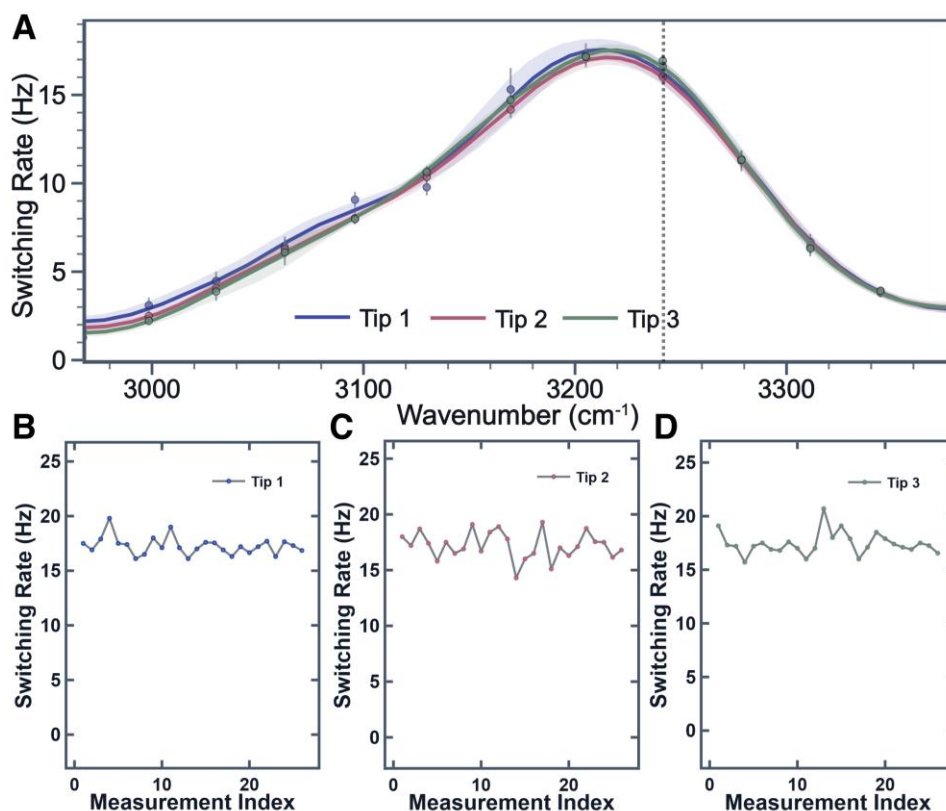


Fig. S11. Tip-dependence of IRiSTM. (A) Action spectra at pyrrolidine $\nu(\text{N-H})$ acquired using three independently prepared STM tips. The well-overlapped curves demonstrated consistent line shapes and spectra intensities (~ 17 Hz), verifying that the identified vibrational features were the intrinsic molecular properties and not sensitive to the macroscopic tip geometries. The error bars and shaded bands represent 99% CI with $N = 36$. The vertical dashed line marks the wavenumber (3205 cm^{-1}) where the data replicates in (B–D) were taken. (B–D) Consecutive switching rate measurements recorded for Tip 1 (B), Tip 2 (C), and Tip 3 (D). Each data point represents the average over 60 s of recording. The results are indistinguishable within experimental error.

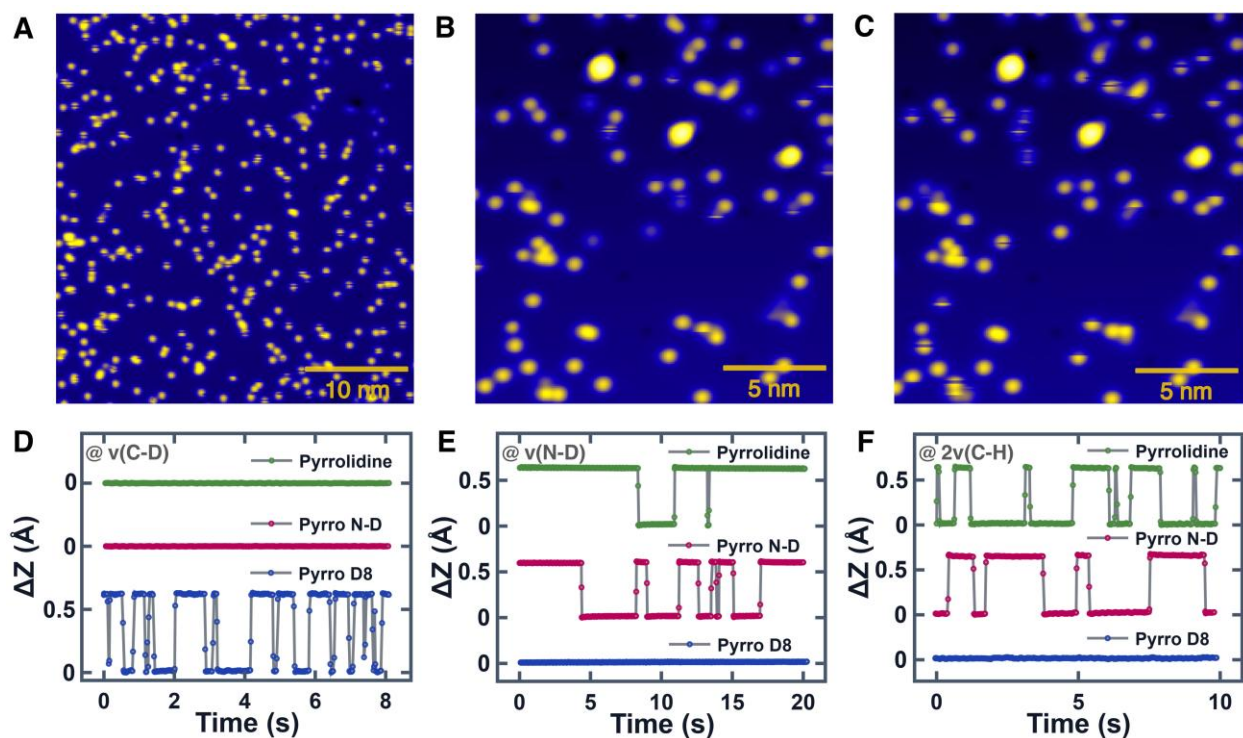


Fig. S12. Isotope-selective identification of pyrrolidine via single-molecule IRiSTM. (A) Large-area STM image with the IR tuned to $\nu(\text{C-D})$, only C-deuterated Pyrro D8 showed stripe-like responses. (B) STM topography while exciting the $\nu(\text{N-D})$. Pyrro N-D molecules were selectively activated, exhibiting a switching rate approximately four times higher than pyrrolidine. To capture these relatively faster dynamics, a smaller scan area with longer pixel dwell time was used. (C) The same area as in (B), imaged under $2\nu(\text{C-H})$ overtone excitation. Both pyrrolidine and Pyrro N-D exhibited enhanced switching. Comparison of (B) and (C) revealed that molecules appearing inactive in (B) but active in (C) corresponded to pyrrolidine. (D-F) Typical ΔZ versus time traces recorded with the STM tip parked over individual molecules to rapidly quantify the switching rates and confirm the identification of pyrrolidine (green), Pyrro N-D (red), and Pyrro D8 (blue) under specific vibrational excitations. The current traces were vertically offset for clarity.

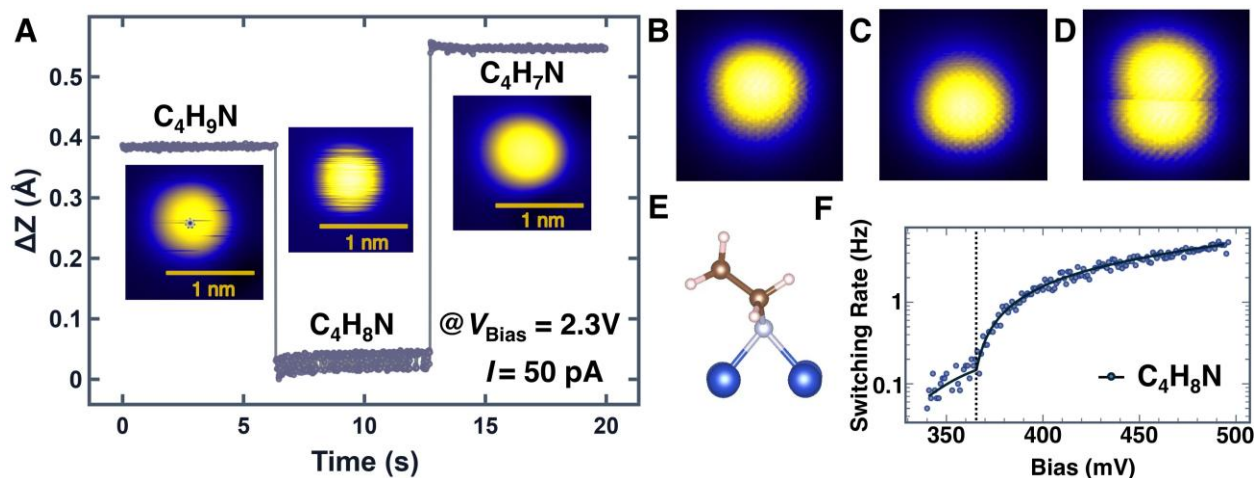


Fig. S13. Stepwise dissociation of pyrrolidine. (A) Real-time ΔZ trace recorded during a high-bias voltage pulse ($V_{\text{bias}} = 2.3$ V, $I = 50$ pA), showing multistep dehydrogenation of a single pyrrolidine molecule. The distinct height change from $\text{C}_4\text{H}_9\text{N}$ to the intermediate $\text{C}_4\text{H}_8\text{N}$ corresponded to the cleavage of the N–H bond. A subsequent step led to a further C-dehydrogenated product. Insets display the STM images of each stage. The black asterisk marks the tip position of the measurement. (B–D) High-resolution STM images characterizing the N-dehydrogenated intermediate $\text{C}_4\text{H}_8\text{N}$. (B) The intermediate in the "Up" state. (C) The molecule in the "Down" state. (D) Captured moment of spontaneous "Up-to-Down" structural transition during scanning. (E) DFT-optimized structure of the $\text{C}_4\text{H}_8\text{N}$ intermediate adsorbed on the Cu(100) surface, showing the N atom bound to Cu bridge sites after N–H dissociation. This calculated geometry is consistent with the observed two-state switching. (F) STM action spectroscopy of the $\text{C}_4\text{H}_8\text{N}$ intermediate. The onset threshold at 367 mV was identified as the $\nu(\text{C–H})$. No features associated with N–H were observed on this product. This further verified that the first dissociation event selectively cleaved the N–H bond.

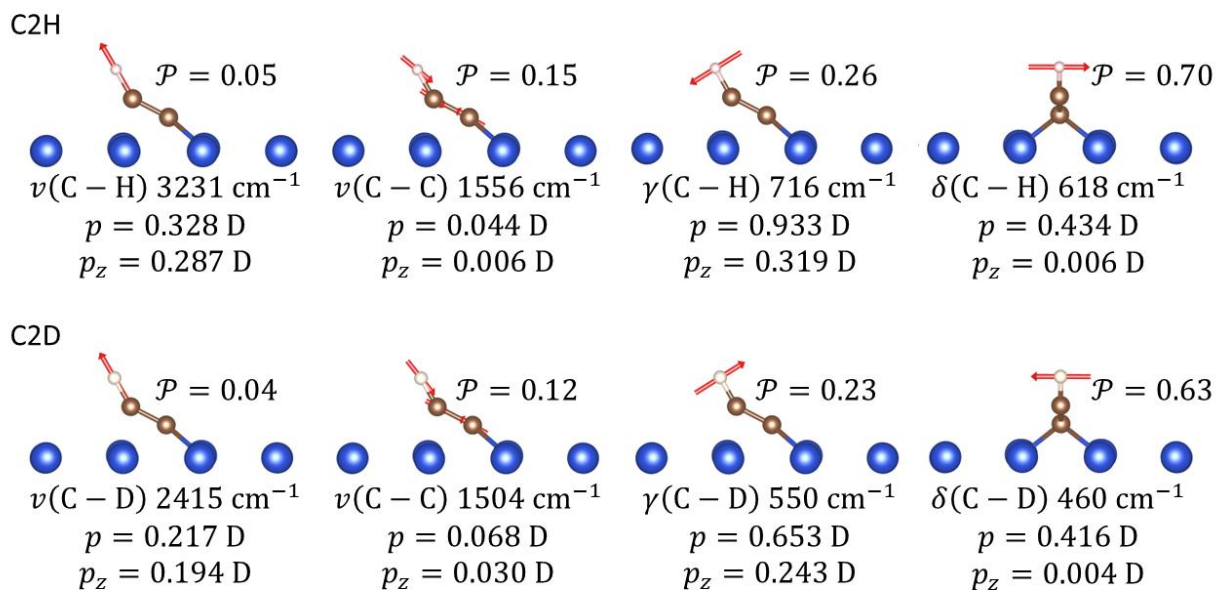


Fig. S14. The simulated vibration modes of C_2H and C_2D . For each mode, the first-order transition dipole moment (p), the component perpendicular to the metal surface (p_z), and the sudden vector projection ($\mathcal{P}$) are labeled. The unit of transition dipole is Debye.

Pyrrolidine

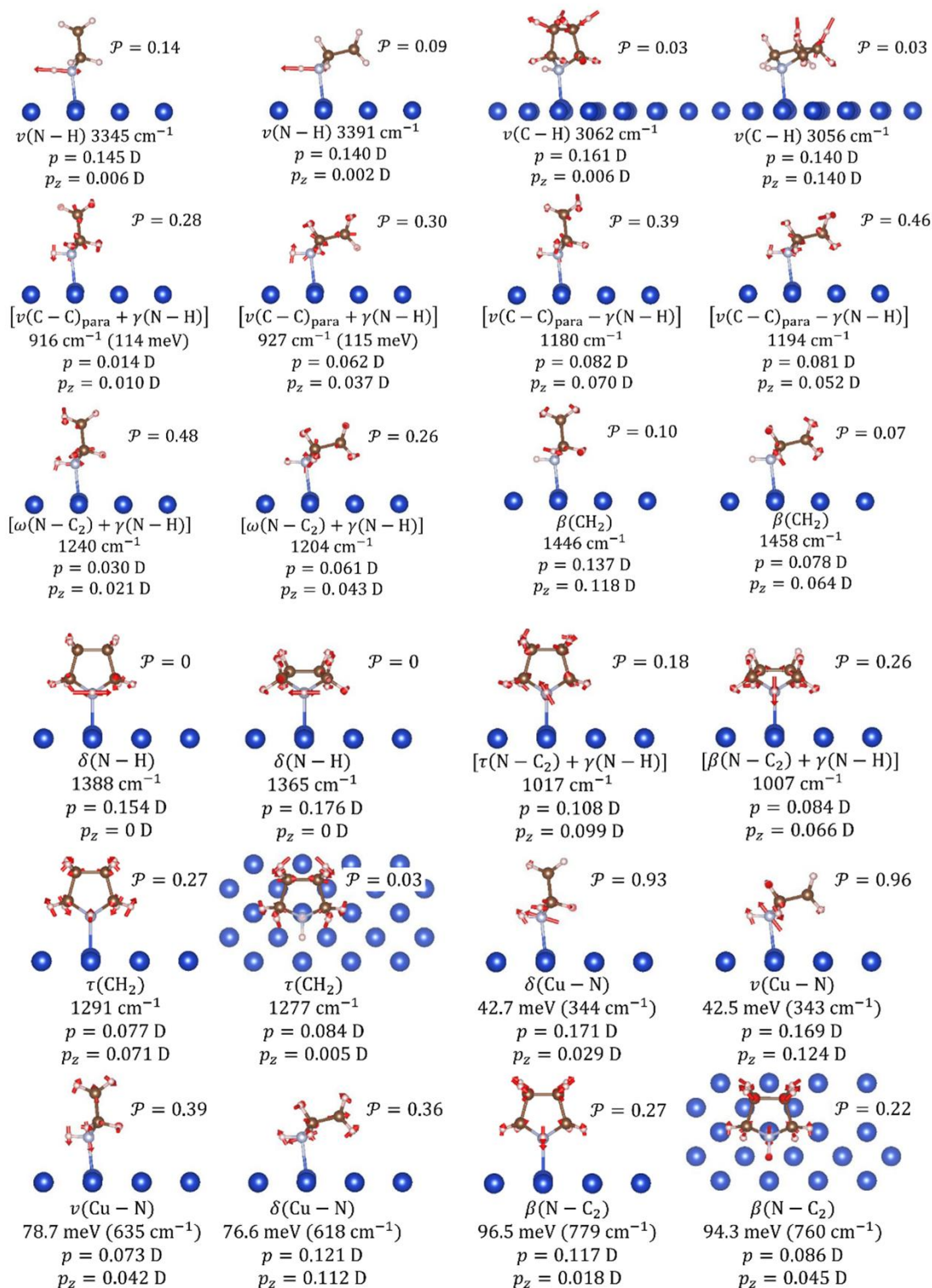


Fig. S15. The simulated vibration modes of pyrrolidine in both configurations. For each mode, the first-order transition dipole moment (p), the component perpendicular to the metal surface (p_z), and the sudden vector projection ($\mathcal{P}$) are labeled. The unit of transition dipole is Debye.

Pyrro D8

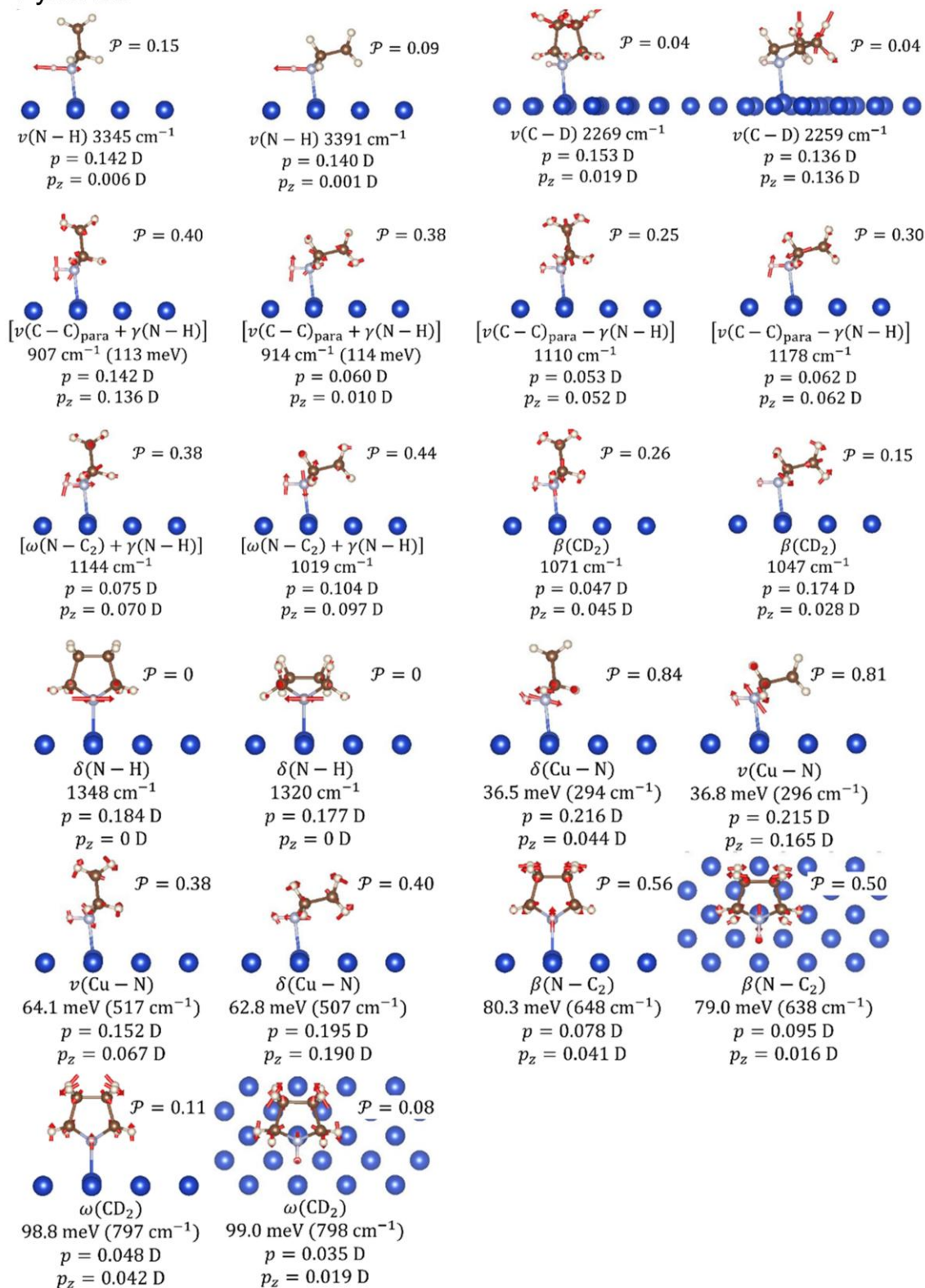


Fig. S16. The simulated vibration modes of Pyrro D8. For each mode, the first-order transition dipole moment (p), the component perpendicular to the metal surface (p_z), and the sudden vector projection (P) are labeled. The unit of transition dipole is Debye.

Pyrro N-D

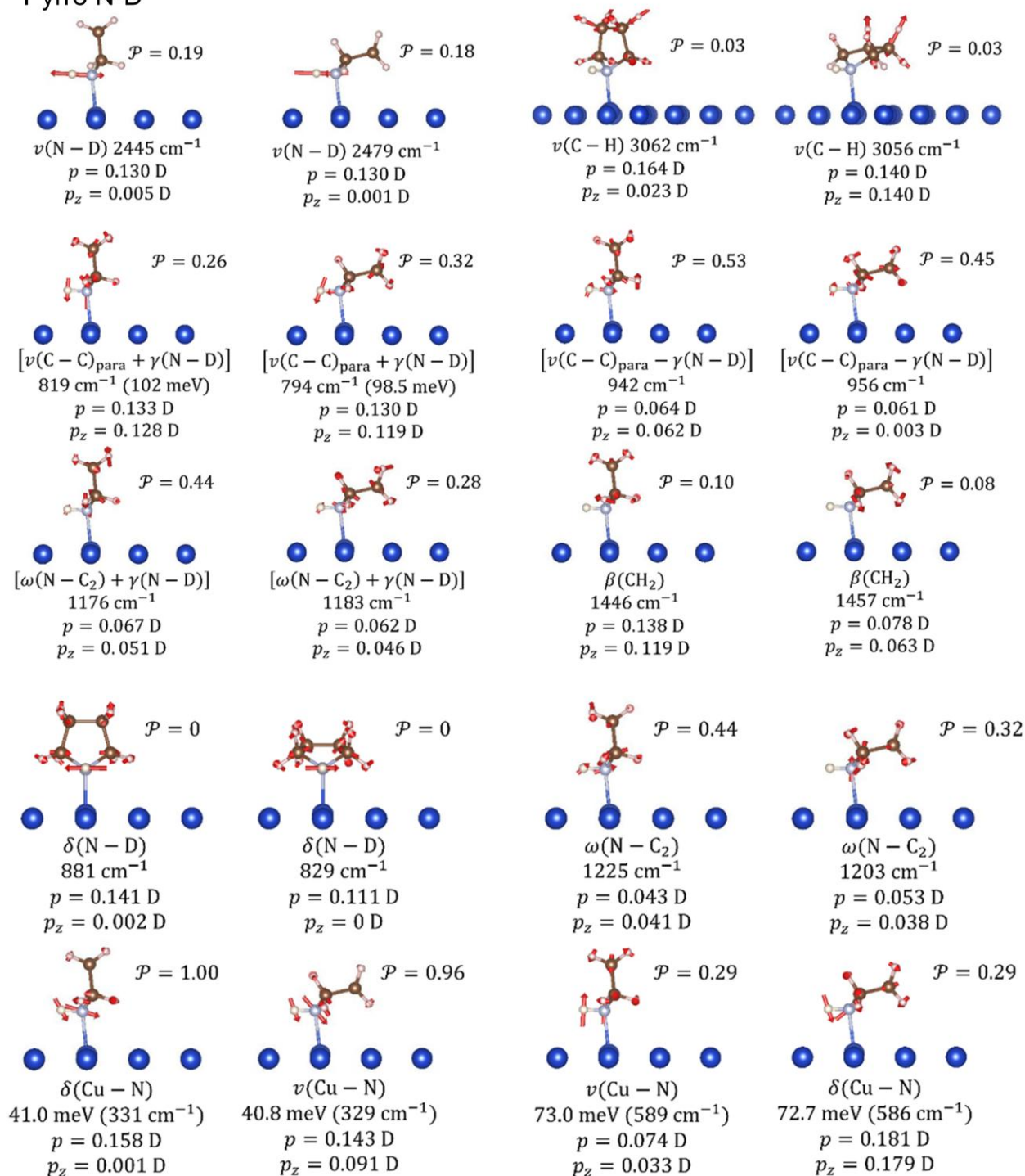


Fig. S17. The simulated vibration modes of Pyrro N-D. For each mode, the first-order transition dipole moment (p), the component perpendicular to the metal surface (p_z), and the sudden vector projection ($\mathcal{P}$) are labeled. The unit of transition dipole is Debye.

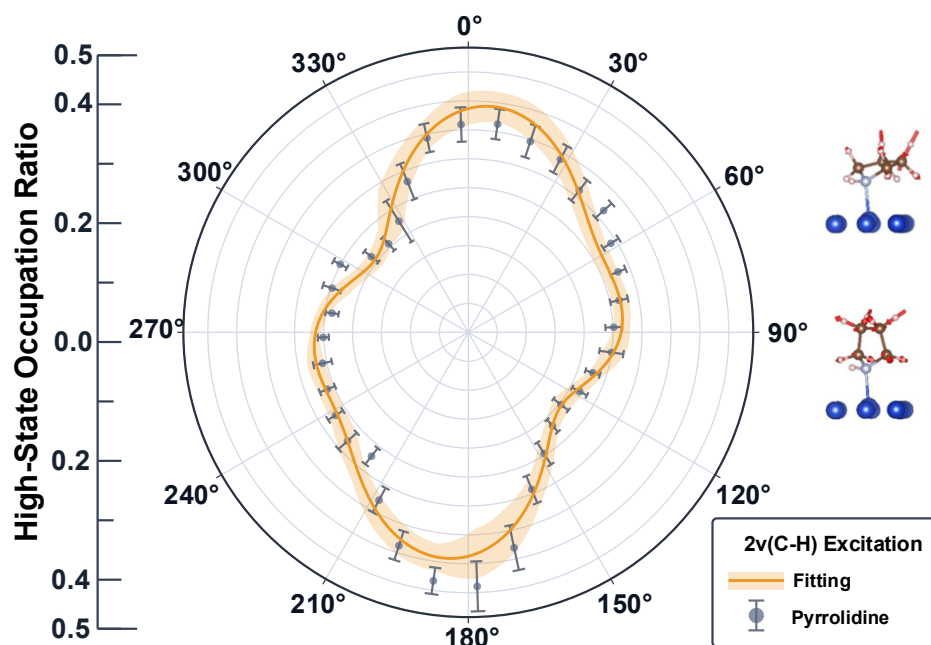


Fig. S18. Polarization Dependence of the “High” State Occupation at 2v(C–H). Here, 0° was defined as p-polarized light with the electric field maximally aligned with the tip Z axis, and the polarization of the incident light was rotated by 360° about the incident direction. Error bars represent the CI with N = 36, the orange shade represents the 99% CI of the central symmetric fitting (orange curve).

Table S1. Vibrational mode assignments for C₂H measured by IRiSTM

Wavenumber / cm ⁻¹	Mode Assignment††	Description
1610	$\nu(\text{C}=\text{C})$	Fundamental C=C stretching
1820	$3\delta(\text{C-H})$	Second overtone of C-H in-plane bending
3160	$\nu(\text{C-H})$	Fundamental C-H stretching
4480	$\nu(\text{C-H}) + 2\delta(\text{C-H})$	Combination band of C-H stretching and the first overtone of C-H in-plane bending
4720	$3\nu(\text{C-C})$	Second overtone of C-C stretching
5100	$\nu(\text{C-H}) + 3\delta(\text{C-H})$	Combination band of C-H stretching and the second overtone of C-H in-plane bending
6310	$2\nu(\text{C-H})$	First overtone of C-H stretching
6500	$4\nu(\text{C-C})$	Third overtone of C-C stretching
6830	$2\nu(\text{C-H}) + \delta(\text{C-H})$	Combination band of the first overtone of C-H stretching and C-H in-plane bending
7000	$4\nu(\text{C-C}) + \delta(\text{C-H})$	Combination band of the third overtone of C-C stretching and C-H in-plane bending
7200	$4\nu(\text{C-C}) + \gamma(\text{C-H})$	Combination band of the third overtone of C-C stretching and C-H out-of-plane bending
7440	$2\nu(\text{C-H}) + 2\delta(\text{C-H})$	Combination band of the first overtone of C-H stretching and the first overtone of C-H in-plane bending
7570	$4\nu(\text{C-C}) + 2\delta(\text{C-H})$	Combination band of the third overtone of C-C stretching and the first overtone of C-H in-plane bending

Table S2. Vibrational mode assignments for C₂D measured by IRiSTM

Wavenumber / cm ⁻¹	Mode Assignment††	Description
1590	$\nu(\text{C}=\text{C})$	Fundamental C=C stretching
1840	$4\delta(\text{C-D})$	Third overtone of C-D in-plane bending
2030	$\nu(\text{C-C}) + \delta(\text{C-D})$	Combination band of C-C stretching and C-D in-plane bending
2325	$\nu(\text{C-D})$	Fundamental C-D stretching
3170	$2\nu(\text{C-C})$	First overtone of C-C stretching
3580	$2\nu(\text{C-C}) + \delta(\text{C-D})$	Combination band of the first overtone of C-C stretching and C-D in-plane bending
4535	$3\nu(\text{C-C})$	Second overtone of C-C stretching
4750	$2\nu(\text{C-D})$	First overtone of C-D stretching
6450	$4\nu(\text{C-C})$	Third overtone of C-C stretching
6870	$4\nu(\text{C-C}) + \delta(\text{C-D})$	Combination band of the third overtone of C-C stretching and C-D in-plane bending
6990	$3\nu(\text{C-D})$	Second overtone of C-D stretching
7190	$\nu(\text{C-D}) + 3\nu(\text{C-C})$	Combination band of C-D stretching and the second overtone of C-C stretching

Table S3. Vibrational mode assignments for pyrrolidine measured by IRiSTM

Wavenumber / cm ⁻¹	Mode Assignment††	Description
1700	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})] + \beta(\text{N-C}_2)$	Combination band of para-position C-C stretching in-phase coupled with N-H out-of-plane bending, plus N-C ₂ scissoring
1860	$2[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	First overtone of the para-position C-C stretching in-phase coupled with N-H out-of-plane bending
2026	$[\omega(\text{N-C}_2) + \gamma(\text{N-H})] + \beta(\text{N-C}_2)$	Combination band of N-C ₂ wagging in-phase coupled with N-H out-of-plane bending, plus N-C ₂ scissoring
2135	$[\omega(\text{N-C}_2) + \gamma(\text{N-H})] + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of N-C ₂ wagging/N-H bending mode and para-position C-C stretching/N-H bending mode
3100	$[\omega(\text{N-C}_2) + \gamma(\text{N-H})] + 2[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of N-C ₂ wagging/N-H bending and the first overtone of para-position C-C stretching/N-H bending
3225	$\nu(\text{N-H})$	Fundamental N-H stretch
3600	$\nu(\text{N-H}) + \delta(\text{Cu-N})$	Combination band of N-H stretching and the Cu-N bending
3700	$3[\omega(\text{N-C}_2) + \gamma(\text{N-H})]$	Third overtone of N-C ₂ wagging in-phase coupled with N-H out-of-plane bending
4480	$3[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})] + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the second overtone of para-position C-C stretching/N-H bending (out-of-phase) and the fundamental mode (in-phase)
4600	$3[\omega(\text{N-C}_2) + \gamma(\text{N-H})] + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the second overtone of N-C ₂ wagging/N-H bending and para-position C-C stretching/N-H bending
4700	$4[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})]$	Fourth overtone of para-position C-C stretching out-of-phase coupled with N-H out-of-plane bending
4800	$3[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})] + [\omega(\text{N-C}_2) + \gamma(\text{N-H})]$	Combination band of the second overtone of para-position C-C stretching/N-H bending and N-C ₂ wagging/N-H bending
5060	$\nu(\text{C-H}) + 2[\tau(\text{N-C}_2) + \gamma(\text{N-H})]$	Combination band of C-H stretching and the first overtone of C-N-C twisting in-phase coupled with N-H bending
5240	$\nu(\text{C-H}) + [\tau(\text{N-C}_2) + \gamma(\text{N-H})] + \tau(\text{CH}_2)$	Three-mode combination: C-H stretching, C-N-C twisting/N-H bending, and methylene twisting
5510	$\nu(\text{C-H}) + 2\tau(\text{CH}_2)$	Combination band of C-H stretching and the first overtone of methylene twisting
5780	$\nu(\text{C-H}) + 2\delta(\text{N-H})$	Combination band of C-H stretching and the first overtone of N-H in-plane bending
5920	$2\nu(\text{C-H})$	First overtone of C-H stretch
6250	$2\nu(\text{N-H})$	First overtone of N-H stretch
6360	$2\tau(\text{CH}_2) + 4[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the first overtone of methylene twisting and the third overtone of C-C/N-H mode
6460	$4[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})] + 2[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the third overtone (out-of-phase) and first overtone (in-phase) of para-position C-C stretching/N-H bending
6970	$2\nu(\text{C-H}) + [\tau(\text{N-C}_2) + \gamma(\text{N-H})]$	Combination band of the first overtone of C-H stretching and C-N-C twisting/N-H bending
7150	$2\nu(\text{C-H}) + [\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})]$	Combination band of the first overtone of C-H stretching and para-position C-C stretching/N-H bending
7460	$2\nu(\text{C-H}) + \beta(\text{CH}_2)$	Combination band of the first overtone of C-H stretching and methylene scissoring

Table S4. Vibrational mode assignments for Pyrro D8 measured by IRiSTM

Wavenumber (cm ⁻¹)	Mode assignment††	Description
1620	$\nu(\text{Cu-N}) + [\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})]$	Combination band of Cu-N stretching and para-position C-C stretching out-of-phase coupled with N-H out-of-plane bending
1820	$2[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	First overtone of para-position C-C stretching out-of-phase coupled with N-H in-plane bending
2070	$\nu(\text{C-D})$	Fundamental C-D stretch
3130	$2[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})] + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the first overtone (out-of-phase) and fundamental (in-phase) of para-position C-C stretching/N-H bending
3225	$\nu(\text{N-H})$	Fundamental N-H stretch
3620	$\nu(\text{N-H}) + \delta(\text{Cu-N})$	Combination band of N-H stretching and the Cu-N bending
4400	$2\nu(\text{C-D})$	First overtone of C-D stretching
4425	$4[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-H})]$	Fourth overtone of para-position C-C stretching in-phase coupled with N-H out-of-plane bending
4600	$4[\omega(\text{N-C}_2) + \gamma(\text{N-H})]$	Fourth overtone of N-C ₂ wagging in-phase coupled with N-H out-of-plane bending
4700	$4[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})] + \beta(\text{CD}_2)$	Combination band of the third overtone of para-position C-C stretching/N-H bending and deuterated methylene scissoring
4780	$4[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})] + [\omega(\text{N-C}_2) + \gamma(\text{N-H})]$	Combination band of the third overtone of C-C/N-H mode and N-C ₂ wagging/N-H bending
4980	$\nu(\text{N-H}) + 2[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of N-H stretching and the first overtone of para-position C-C stretching/N-H bending
5130	$2\nu(\text{C-D}) + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-H})]$	Combination band of the first overtone of C-D stretching and para-position C-C stretching/N-H bending
5240	$2\nu(\text{C-D}) + \beta(\text{CD}_2)$	Combination band of the first overtone of C-D stretching and deuterated methylene scissoring
5570	$2\nu(\text{C-D}) + \delta(\text{N-H})$	Combination band of the first overtone of C-D stretching and N-H in-plane bending
5900	$\nu(\text{N-H}) + 2\delta(\text{N-H})$	Combination band of N-H stretching and the first overtone of N-H in-plane bending
6250	$2\nu(\text{N-H})$	First overtone of N-H stretching
6375	$3\nu(\text{C-D})$	Third overtone of C-D stretching
6880	$3\nu(\text{C-D}) + \nu(\text{Cu-N})$	Combination band of the second overtone of C-D stretching and Cu-N stretching
7000	$3\nu(\text{C-D}) + \beta(\text{N-C}_2)$	Combination band of the second overtone of C-D stretching and N-C ₂ scissoring
7470	$3\nu(\text{C-D}) + \beta(\text{CD}_2)$	Combination band of the second overtone of C-D stretching and deuterated methylene scissoring

Table S5. Vibrational mode assignments for Pyrro N-D measured by IRiSTM

Wavenumber (cm ⁻¹)	Mode assignment ^{††}	Description
1620	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})] + [\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-D})]$	Combination band of para-position C-C stretching out-of-phase and in-phase coupled with N-D out-of-plane bending
2026	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})] + \omega(\text{N-C}_2)$	Combination band of para-position C-C stretching/N-D bending (in-phase) and N-C ₂ wagging
2134	$[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-D})] + \omega(\text{N-C}_2)$	Combination band of para-position C-C stretching/N-D bending (out-of-phase) and N-C ₂ wagging
2300	$\nu(\text{N-D})$	Fundamental N-D stretch
3100	$2[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-D})] + \omega(\text{N-C}_2)$	Combination band of the first overtone of para-position C-C stretching/N-D bending and N-C ₂ wagging
3280	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})] + 2[\omega(\text{N-C}_2) + \gamma(\text{N-D})]$	Combination band of C-C/N-D mode and the first overtone of N-C ₂ wagging/N-D bending
3600	$2[\omega(\text{N-C}_2) + \gamma(\text{N-D})] + \omega(\text{N-C}_2)$	Combination band of the first overtone of N-C ₂ wagging/N-D bending and N-C ₂ wagging
3700	$3\omega(\text{N-C}_2)$	Third overtone of N-C ₂ wagging
4480	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})] + 3[\omega(\text{N-C}_2) + \gamma(\text{N-D})]$	Combination band of C-C/N-D mode and the second overtone of N-C ₂ wagging/N-D bending
4600	$[\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})] + 3\omega(\text{N-C}_2)$	Combination band of C-C/N-D mode and the second overtone of N-C ₂ wagging
4600	$2\nu(\text{N-D})$	First overtone of N-D stretching
4700	$4[\omega(\text{N-C}_2) + \gamma(\text{N-D})]$	Fourth overtone of N-C ₂ wagging in-phase coupled with N-D out-of-plane bending
4800	$3[\omega(\text{N-C}_2) + \gamma(\text{N-D})] + \omega(\text{N-C}_2)$	Combination band of the second overtone of N-C ₂ wagging/N-D bending and N-C ₂ wagging
5130	$\nu(\text{C-H}) + \delta(\text{N-D}) + \tau(\text{CH}_2)$	Three-mode combination: C-H stretching, N-D in-plane bending, and methylene twisting
5240	$\nu(\text{C-H}) + \delta(\text{N-D}) + \beta(\text{CH}_2)$	Three-mode combination: C-H stretching, N-D in-plane bending, and methylene scissoring
5510	$\nu(\text{C-H}) + 2\tau(\text{CH}_2)$	Combination band of C-H stretching and the first overtone of methylene twisting
5780	$\nu(\text{C-H}) + 2\beta(\text{CH}_2)$	Combination band of C-H stretching and the first overtone of methylene scissoring
5920	$2\nu(\text{C-H})$	First overtone of C-H stretching
6360	$2[\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-D})] + 4\omega(\text{N-C}_2)$	Combination band of the first overtone of C-C/N-D mode (out-of-phase) and the third overtone of N-C ₂ wagging
6500	$2\nu(\text{C-H}) + \nu(\text{Cu-N})$	Combination band of the first overtone of C-H stretching and Cu-N stretching
6720	$2\nu(\text{C-H}) + [\nu(\text{C-C})_{\text{para}} + \gamma(\text{N-D})]$	Combination band of the first overtone of C-H stretching and C-C/N-D mode (in-phase)
6950	$2\nu(\text{C-H}) + [\nu(\text{C-C})_{\text{para}} - \gamma(\text{N-D})]$	Combination band of the first overtone of C-H stretching and C-C/N-D mode (out-of-phase)
6950	$2\nu(\text{C-H}) + [\omega(\text{N-C}_2) + \gamma(\text{N-D})]$	Combination band of the first overtone of C-H stretching and N-C ₂ wagging/N-D bending
7400	$3\nu(\text{N-D})$	Third overtone of N-D stretching
7460	$2\nu(\text{C-H}) + \beta(\text{CH}_2)$	Combination band of the first overtone of C-H stretching and methylene scissoring

^{††}**Notation:** ν = stretching, ν_{as} = asymmetric stretching, γ = out-of-plane bending, β = scissoring, ω = wagging, τ = twisting. Para = para-position (used for C-C bonds). Square brackets [] group coupled vibrations: [+] indicates in-phase coupling, [-] indicates out-of-phase coupling. [] + [] denotes a combination band of two modes. $n[]$ represents the (n-1)th overtone of the bracketed mode ($n = 2, 3, 4$). CH₂ = methylene group, N-C₂ = carbon-nitrogen-carbon bond.