Rotation of a single acetylene molecule on Cu(001) by tunneling electrons in STM

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We study the elementary processes behind one of the pioneering works on STM controlled reactions of single molecules [Stipe et al., Phys. Rev. Lett. 81, 1263 (1998)]. Using the Keldysh-Green function approach for the vibrational generation rate in combination with DFT calculations to obtain realistic parameters we reproduce the experimental rotation rate of an acetylene molecule on a Cu(100) surface as a function of bias voltage and tunneling current. This combined approach allows us to identify the reaction coordinate mode of the acetylene rotation and its anharmonic coupling with the C-H stretch mode. We show that three different elementary processes, the excitation of C-H stretch, the overtone ladder climbing of the hindered rotational mode, and the combination band excitation together explain the rotation of the acetylene molecule on Cu(100).

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Tunneling electrons from a scanning tunneling microscope (STM) form an atomic source of electrons for electronic and vibrational excitations which can be used to manipulate individual atoms and molecules in a controlled manner. The study of acetylene C2H(D)2 rotation on the Cu(001) surface was the first comprehensive and systematic experiment on a single adsorbate manipulation made in combination with STM inelastic electron tunneling spectroscopy (STM-IETS). This method has been established as an indispensable experimental method to gain insight into the vibrationally mediated motions and reactions of single molecules with STM (see, e.g., Ref. 6 and references therein).

The observed in Ref. 5 rotation yield per electron as a function of bias voltage for C2H2(D2) exhibits a threshold at 358 (266) mV. This corresponds to the excitation of the CH(D) stretch mode which is not a rotational mode. In this respect it is very different from, e.g., the rotation of a single oxygen molecule on Pt(111) surface, where the hindered rotational mode can be directly excited by tunneling electrons.

That the onset of a molecular motion/modification is caused by a vibrational mode that is not directly responsible for the observed motion is not unique. Many other examples have been established, e.g., the migration of CO on Pd(110)8. The rotation of C2H(D)2/Cu(001) also demonstrates several peculiar features which have not been previously understood. In this paper we revisit the experimental findings of Ref. 5. Based on DFT calculations and the Keldysh diagram technique we clarify the vibrational modes and elementary physical processes behind the characteristic features of the acetylene rotation on Cu(001).

The experimental data on the C2H2/Cu(001) rotation is summarized as symbols in Figs. 1 and 2(a). The higher threshold at 358 meV, see Fig. 1, corresponds to excitation of the CH stretch mode. In addition, a lower threshold with a much smaller rotation yield is clearly seen at ~ 240 meV, we note that this does not correspond to any vibrational energy of the C2H2/Cu(001), see below. The third feature is the crossover from a single to two-electron process with increasing tunneling current above 10 nA, see Fig 2(a). This crossover cannot be attributed to a resonant inelastic electron-molecule scattering with rotational excitation as in the case of O2/Pt(111), because of the evident absence of direct excitation of the hindered rotational modes. Moreover, the crossover cannot be attributed to coherent ladder climbing since the reaction order (number of electrons needed) does not approach one at high bias5,10.

The identification of the precursor to rotation is not straightforward since the molecule has a number of low frequency vibrational modes. The hindered rotational mode of C2H2 on Cu(001) ~ 28 meV, whereas the thermally measured barrier for rotation is relatively high εθ = 169 ± 3 meV12. For this low-energy rotational mode to directly induce rotations, a multi (5-6)-electron processes is expected, whereas in the experiment, as explained above, only a two-electron process is observed at larger tunneling currents.

To analyse the mechanisms of rotation of a single C2H2/Cu(001) by tunneling electrons we performed DFT cal-

FIG. 1. Rotation yield per electron as a function of bias voltage at fixed tunneling current I = 40 nA. Circles are experimental data from Ref. 5. Blue dashed line is the linear process A, Eq. (1), red dash-dotted line is the nonlinear process B, Eq. (1), and green dotted line is the combination band process C, Eq. (11). Black solid line corresponds to a sum of all processes. Lines are calculated via Eqs. (12) with A = 2.5 × 10−6, B = 6 × 10−16, C = 1.2 × 10−8, and Γel(Ω1), the CH mode generation rate Eq. (3), is calculated via the Keldysh technique, the parameters are specified in the text.
FIG. 2. Rotation yield per electron $Y$ as a function of tunneling current (panel a). Symbols show the experimental data from Ref. 3. Lines are the calculated results for different bias voltages: $V = 400$ (black solid line), 449 (red dashed), 500 (green dash-dotted), and 600 mV (blue dotted). Thin dash-dotted lines are the linear and nonlinear contributions to the rotation yield for $V = 600$ mV. The calculations are done with the same parameters as in Fig. 1. The dependencies of the hybridization parameter $\Delta$ on current for different bias voltages are shown in panel b.

### Table I. Calculated/experimental vibrational energies, damping rates, and angular momentum of C$_2$H$_2$ on Cu(001). The frustrated rotational modes along (001) are emphasized in bold.

| $\nu$ | Mode | $h\Omega_i$ meV | $\gamma_i^{(v)}$ $10^{-12} s^{-1}$ | $L_i^{(v)}$ (rel.u.) | $\gamma_i^{(v)}$ | $L_i^{(v)}$ |
|-------|------|----------------|-------------------------------|--------------------|----------------|--------------------|
|       |      | theory expt work | theory expt work | Ref. 1 | Ref. 14 | Ref. 5 | this work |
| 1     | CH stretch sym | 371 379 364 358 | 1.0 | 0.01 | 0.01 | 0 |
| 2     | CH stretch asym | 368 375 357 358 | 0.7 | 1.66 | -1.66 | 0 |
| 3     | CC stretch | 167 171 164 N.O.** | 2.2 | 0 | 0 | 0 |
| 4     | CH in-plane bend or wag, asym | 131 132 141 N.O. | 0.2 | 1.16 | -1.16 | 0 |
| 5     | CH in-plane bend or scissor, sym | 111 117 118 N.O. | 1.5 | 0 | 0 | 0 |
| 6     | CH out-of-plane bend or asym rotation | 100 101 78 N.O. | 0.7 | 0 | 0 | -1.06 |
| 7     | out-of-plane bend or cartwheel | 71 75 N.O. | 0.2 | -0.24 | -0.24 | 0 |
| 8     | in-plane bend or wag | 58 N.P.* | 2.0 | 1.26 | -1.26 | 0 |
| 9     | molecule-Cu stretch | 50 N.P. | 0.05 | 0 | 0 | 0 |
| 10    | in-plane rotation | 29 N.P. | 1.8 | -0.35 | 0.35 | 0 |
| 11    | out-of-plane rotation | 28 N.P. | 0.2 | 0 | 0 | 1 |
| 12    | out-of-plane bend | 23 N.P. | 0.04 | -0.04 | -0.05 | 0.03 |

* N.P.: Not Published
** N.O.: Not Observed

Calculations on a 4x4 Cu(001) surface with one adsorbed acetylene molecule. The calculations of relaxed geometries, vibrational energies, and electron-hole pair damping rates were carried out with SIESTA. Other details of the DFT calculations are presented in the Supplementary Material, Sec. I (SM-I in what follows). We also estimated the energy barrier $\epsilon_B$ for C$_2$H$_2$ rotation on Cu(001) to 100 meV using the nudged elastic band method.

The results for the vibrational energies $h\Omega_i$ and electron-hole damping rates $\gamma_i^{(v)}$, $\nu = 1$,...,12 are given in Tab. I in comparison with the previous theoretical and experimental results. The last three columns of Tab. I show (in relative units) the components of each mode angular momentum $L_i^{(v)} = \sum \Omega_i (\vec{r}_i - \vec{r}_{CM}) \times m_i \delta r_i^{(v)}$, where $\vec{r}_i$, $m_i$ are the atomic positions (in the acetylene molecule) and masses, $\vec{r}_{CM}$ the center-of-mass, and $\delta r_i^{(v)}$ the atomic displacements in the vibrational mode $v$. The high frequency modes (# 1 & 2 in Tab. I) are the symmetric and antisymmetric CH stretch modes. The higher threshold energy of the rotation yield $Y(V) = R(V)/R(0)$ at 358 mV and the corresponding peak in the $\Delta \log(Y)/\Delta V$ plot, observed in Ref. 4, indicates that inelastic excitation by tunneling electrons of these modes is a trigger for rotation. Along the reaction pathway there are only two frustrated rotation modes which has angular momentum in the (001) direction, # 6 and # 11.

The full Hamiltonian of the system can be written as a sum of the electronic and vibrational (phonon) parts,

$$H = H_e(\delta q_i) + H_{ph},$$

(1)

where the electronic part $H_e$ depends on the normal coordinates of the molecule $\delta q_i$. Using the Newns-Anderson type Hamiltonian, we write

$$H_e = \epsilon_a (\delta q_i) c_a^\dagger c_a + \sum_{j,l,s} \epsilon_j c_j^\dagger c_j + \sum_{j,l,s} V_l (c_j^\dagger c_a + h.c.),$$

(2)

where the indices $l(t)$ and $a$ denote a substrate (tip) and the adsorbate, respectively; the corresponding energy levels are $\epsilon_{a(t)}(\delta q_i)$. Electronic tunneling matrix elements $V_l$ (tip-adsorbate) and $V_s$ (substrate-adsorbate) give rise to a stationary tunneling current between the tip and the substrate through the adsorbate orbital at applied bias voltage $V$. The electron occupation functions in the substrate and tip are assumed to be Fermi distributions with the same temperature $T$ but different chemical potentials $\mu_t$ and $\mu_s$, $\mu_s - \mu_t = eV$.

In order to clarify the interaction parts of the full Hamiltonian (1) behind the experimental results on the acetylene rotation, it is convenient to split the rotation rate into three partial processes,

$$R(V) = R_A(V) + R_B(V) + R_C(V),$$

(3)

where the rates $R_A(V)$ and $R_B(V)$ are, respectively, the one- and two-electron processes with a higher threshold $V \sim 358$ mV, and $R_C(V)$ is the one-electron process with a lower threshold $V \sim 240$ mV.

To describe the generation of high frequency CH stretch modes, the adsorbate orbital energy in the 1st term of Eq. (2) can be expanded\textsuperscript{18} to the first order as

$$\epsilon_a(\delta q_i) \approx \epsilon_a(0) + \chi (b_h^\dagger + b_h),$$

(4)

where $\chi$ is an electron-phonon constant and $\epsilon_a(0)$ the unperturbed adsorbate energy, $b_h$ is the annihilation operator of the vibrational mode $\delta q_h = 2^{-1/2} (b_h^\dagger + b_h)$ with the frequency $\Omega_h = 358$ meV, which is directly excited by the inelastic tunneling current\textsuperscript{19}.

The high frequency vibration generation rate then reads\textsuperscript{3}

$$\Gamma_{set}(\Omega_h, V) = \int d\omega \Gamma_{ph}^{(h)}(\omega) \gamma_{in}(\omega, \Omega_h, V),$$

(5)
where \( \rho_{ph}^{(h)}(\omega) = \frac{1}{\pi} \frac{\gamma_{eh}^{(h)}}{(\omega - \Omega_h)^2} + \left(\frac{\gamma_{eh}^{(h)}}{\Delta_h}\right)^2 \), \( \gamma_{eh}^{(h)} \) is the inverse lifetime of the phonon mode \( h \) due to electron-hole pair excitation, given in Table II. At \( T = 0 \),

\[
\Gamma_{in}(\omega, \Omega_h, V) = \frac{\gamma_{eh}^{(h)}}{\hbar\Omega_h} \left( |eV| - \hbar\omega \right) \Theta \left( \frac{|eV|}{\hbar\omega} - 1 \right). \tag{6}
\]

Our next task is to find the mechanisms of the energy transfer between the high frequency CH stretch mode and the reaction coordinate (RC) hindered rotational mode. The first possibility is the direct over-barrier rotation excitation due to an inelastic tunneling generation of the stretch mode \( \Omega_{h,2,1} \). The rotation rate corresponding to such single-electron process can be described \(^{22}\) as a linear function of the CH stretch mode generation rate,

\[
R_A(V) = A \Gamma_{in}(\Omega_h, V). \tag{7}
\]

A good fit to the experimental data is given by \( A = 2.5 \times 10^{-6} \), see Fig. IV. The physical meaning of \( A \) is the probability of a CH stretch vibration to excite the \( \text{C}_2\text{H}_2 \) rotation over the barrier. This value is in reasonable agreement with the well established case of the migration of CO on Pd(110)\(^{8,23}\). However, this mechanism cannot describe the two-electron process. In principle, the direct over-barrier rotation excitation from the second excited level of the CH stretch mode provides a two-electron process. However, this process can be discounted since the short lifetime \( (\gamma_{eh}^{(h)})^{-1} \sim 1 \) ps gives a nearly two orders of magnitude smaller rate.

Another possibility for the energy transfer is an anharmonic interaction of the CH stretch mode with the reaction coordinate mode. In the simplest case this can be described as a cubic coupling. We expand the vibrational Hamiltonian \( H_{ph} \) in Eq. (I) up to cubic terms to account for the coupling between the directly excited \( (\nu = h) \) and the reaction coordinate \( (\nu = r) \) modes,

\[
H_{ph} = H_0 + H_{ph,1} + H_{ph,2} \equiv \sum_{\nu=\text{h,r},i} \hbar \Omega_\nu b_\nu^\dagger b_\nu + K_{h,r,i}(b_\nu^\dagger b_i^\dagger b_h + h.c.) + \frac{1}{2} K_{h,r,r}(b_i^\dagger b_i^\dagger b_h + h.c.), \tag{8}
\]

where \( K_{h,r,i} \) and \( K_{h,r,r} \) are the anharmonic coupling constants, and \( \nu = i \) is possibly some auxiliary (idler) vibrational mode excited simultaneously with the RC mode.

DFT calculation of the anharmonic coupling constants is prohibitively time-consuming. We therefore construct (see in SM-II and III) a simpler model which takes into account only the pair interactions between the nearest neighbors as springs on rods; the results for the coupling coefficients are shown as colors in Fig IV. The symmetric CH stretch mode #1 couples most efficiently with a pair of the asymmetric rotations #6. In contrast, asymmetric CH stretch mode #2 couples strongly with a pair of non-equivalent phonons, i.e., asymmetric rotation #6 and cartwheel mode #7. The coupling to the symmetric rotation mode #11 is ineffective and the coefficients are approximately two orders of magnitude smaller. Thus, the asymmetric rotation #6 (CH out-of-plane bend) is the most probable candidate for being the acetylene/Cu(001) rotation precursor.

Two different pathways responsible for the two-electron partial process \( R_B \) are possible. If the barrier height is \( \epsilon_B > 2\Omega_r \), only the second term in Eq. (8) contributes. In this case the rotation starts from the excitation of the high energy symmetric CH stretch mode #1 and two successive decays into pairs of RC mode (#6) are needed to overcome the barrier. Such an overtone ladder climbing process (see Fig. IV) was first discussed for a desorption of CO molecules in Ref. 4.

If \( \Omega_r < \epsilon_B < 2\Omega_r \), one pair of the RC stretch excitations is enough to cross the barrier which just gives a correction to the single-electron rate \( R_A \). In this case, the only possibility for a two-electron process comes from the third term in Eq. (8). The rotation starts from the excitation of the high energy anti-symmetric CH stretch mode (#2), and two successive decays into pairs of RC mode (#6) and idler mode (#7) are needed to overcome the barrier. This corresponds to the usual single-step ladder climbing process \(^{20}\).

In both cases the generation rate of RC phonons (pairs of phonons) is proportional to the generation rate of the CH stretch phonons, \( \Gamma_{in}(\Omega_r, V) \propto \Gamma_{in}(\Omega_h, V) \) (see more detail in SM-IV). Analysing the Pauli master equations for the one- and two-step RC potential ladder climbing processes shows that the rotation rate is

\[
R_B(V) = B \Gamma_{in}^2(\Omega_r, V), \tag{9}
\]

with different formulas for the coefficient \( B \) depending on the corresponding anharmonic coupling coefficients \( K \) and the ratio of the RC and idler modes linewidth to the detuning \( \Omega_h - \Omega_r - \Omega_i \) (\( \Omega_h - 2\Omega_r \)), because the anharmonic decay of the stretch mode is nonresonant, see SM-V.

The fitted value \( B = 6 \times 10^{-16} \) s reproduce the experimental data above the higher threshold \( \sim 360 \) mV well, see Fig. IV. The hybridizations parameters \( \Delta_i = 200 \) meV, \( \Delta_r = 12 \) meV were fixed from the tunneling current \( I(\Omega_h) = 40 \) nA and the fraction of the inelastic component \( I_{inel}/I \approx 1\% \) at \( V = 400 \) mV. To simulate higher current levels, the same parameters were used except \( \Delta_i \) which changes as a function of bias and tunneling current as shown in Fig. IV(b). The calculated rotation rate as a function of tunneling current underlines the
The anharmonic coupling coefficients described above allows for a theoretical estimation of $B$. If $\Omega_r < \varepsilon_B < 2\Omega_r$, the estimate is $B = 3.5 \times 10^{-15} \text{s}$, which is about 7 times larger than the best fit value. However, as noted above, the double excitation of the reaction coordinate mode gives in this case a contribution to $R_A(V)$. The resulting value of the coefficient $A$ is then $6 \times 10^{-3}$, i.e., $10^3$ times larger than the fitted value $2.5 \times 10^{-6}$. This allows us to exclude the case of a lower rotational barrier from consideration since it would give rise to a much faster one-electron process than seen experimentally. The only possibility left is that $\varepsilon_B > 2\Omega_r$. The theoretical estimate for $B$ is then $\sim 2.4 \times 10^{-14} \text{s}$, i.e., approximately 5 times larger than the fitted value. We believe, due to approximations, this value to be in reasonable agreement with the experiment.

As can be seen from Fig. 1 below the higher energy threshold $\Omega_b$ the rotation rate per electron is very low but non zero above a lower threshold of $\sim 240 \text{ meV}$. This can be attributed to an inelastic electron tunneling processes which involves a simultaneous combination band$^{25}$ generation of two coherent phonons $\nu = c_1, c_2$. Assuming that the adsorbate energy in Eq. (2) is now a function of these vibrational modes, $\varepsilon_d(\nu; q_{c_1}, q_{c_2})$, and expanding it in a Taylor series

$$
\varepsilon_d(\nu; q_{c_1}, q_{c_2}) = \varepsilon_d(0) + \eta(b_{c_1} + b_{c_2})(b_{c_1}^\dagger + b_{c_2}^\dagger),
$$

where $\eta = \frac{\partial^2 \varepsilon_d(0)}{\partial q_{c_1} \partial q_{c_2}}$ and, $b_{c_1}$ and $b_{c_2}$ are annihilation operators of the vibrational modes with frequencies $\Omega_{c_1}$ and $\Omega_{c_2}$, and $eh$ damping rates $\gamma_{eh}^{(c_1)}, \gamma_{eh}^{(c_2)}$. The analysis of this mechanism using the Keldysh-Green’s functions shows that the total coherent phonon excitation rate takes the form of a single-phonon excitation rate $\Gamma_{\nu e}(\Omega, V)\varepsilon_d(0)$, Eq. (3), where a single vibrational frequency is simply replaced by the sum of two vibrational frequencies. This gives for the reaction rate, instead of Eq. (7),

$$
R_{c}(V) = C \Gamma_{\nu e}(\Omega_{c_1} + \Omega_{c_2}, V),
$$

where $\Gamma_{\nu e}(\Omega_{c_1} + \Omega_{c_2}, V) = \frac{\gamma_{eh}^{(c_1)} + \gamma_{eh}^{(c_2)}}{\Omega_{c_1} + \Omega_{c_2}} \Delta \left(\frac{|eV|}{\Omega_{c_1} + \Omega_{c_2}} - 1\right)$ and the coefficient $C$ depends on the parameters of the system as explained in $\text{SM}-\text{VI}$. Although it is difficult to make a theoretical estimate of this coefficient, the fitted value to the experimental data is $C = 12.2 \times 10^{-8}$. Thus, the combination band single-electron process is about $A/C \sim 200$ slower than the process with rotation excitation via CH stretch vibration. This is in reasonable agreement with the fact that the process Eq. (11) occurs in the next order of the perturbation theory compared with the process Eq. (4).

The over-barrier rotation mode excitation occurs due to an inelastic tunneling generation of a coherent pair of phonons, e.g. the in-plane bend or wag mode $\Omega_{c_1} = 141 \text{ meV}$ and in-plane bend or scissor mode $\Omega_{c_2} = 118 \text{ meV}$ (modes # 4 and 5). Another possibility is that the second of these phonons is the asymmetric out-of-plane rotation $\Omega_{c_2} = 101 \text{ meV}$ (mode #6). The latter, being a hindered rotation mode, may simplify the resulting molecule rotation.

To conclude, we show that the precursor for the acetylene rotation on Cu(001) is the out-of-plane bend (or asymmetric rotation) mode $\sim 100 \text{ meV}$ (#6 in Table I). Rotation with a higher threshold voltage $358 \text{ mV}$ occurs if enough energy stored in the high-frequency CH stretch mode excited by tunneling electrons is transferred to the rotational mode (reaction coordinate). The anharmonic coupling of the CH mode with the hindered rotation mode is found to be responsible for a crossover from a single to multiple electron process for tunneling currents higher than $10 \text{ nA}$. The lower threshold voltage for rotation at $240 \text{ mV}$ is attributed to a combination band process of inelastic scattering of tunneling electrons on a pair of lower-energy vibrational excitations of the acetylene molecule.

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Current-Driven Phenomena in Nanoelectronics, edited by T. Seideman (Pan Stanford Publishing Pte. Ltd., 2011) Chap. 2, pp. 26–89.

7 D. Teillet-Billy, J. P. Gauyacq, and M. Persson, Phys. Rev. B 62, R13306 (2000).
8 T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, and H. Ueba, Science 295, 2055 (2002).
9 Rotation of C$_2$D$_2$ on Cu(001) will be analyzed elsewhere, it can be done analogously to the current approach.
10 G. P. Salam, M. Persson, R. E. Palmer, Phys. Rev. B 49, 10655 (1994).
11 S. G. Tikhodeev and H. Ueba, Phys. Rev. B 70, 125414 (2004).
12 L. J. Lauhon and W. Ho, J. Chem. Phys 111, 5633 (1999).
13 F. E. Olsson, M. Persson, N. Lorente, L. J. Lauhon, W. Ho, and P. Sabatier, J. Phys. Chem. B 106, 8161 (2002).
14 T. Marinova and P. K. Stefanov, Surf. Sci. 191, 66 (1987).
15 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).
16 T. Frederiksen, N. Lorente, M. Paulsson, and M. Brandbyge, Phys. Rev. B 75, 235441 (2007).
17 D. M. Newns, Phys. Rev. 178, 1123 (1969).
18 B. N. J. Persson and M. Persson, Solid State Comm. 36, 175 (1980).
19 Actually the energies of the high frequency CH stretch modes are slightly different, see in Table II we will use this experimental value from Ref.5 in the estimates below.
20 S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. B 55, 4825 (1997).
21 B. N. J. Persson and H. Ueba, Surf. Sci. 502, 18 (2002).
22 T. Kumagai, A. Shiotari, H. Okuyama, S. Hatta, T. Aruga, I. Hamada, T. Frederiksen, and H. Ueba, Nat. Materials 11, 167 (2012).
23 H. Ueba, Phys. Rev. B 86, 035440 (2012).
24 S. Gao, Surf. Sci. 313, 448 (1994).
25 P. Jakob and B. N. J. Persson, J. Chem. Phys 109, 8641 (1998).
Rotation of a single acetylene molecule on Cu(001) by tunneling electrons in STM: Supplementary Materials

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The details are given for

• DFT calculation of the vibrational modes of acetylene molecule on Cu(001) surface and the inelastic tunneling;
• Third order anharmonic terms in the vibrational Hamiltonian which are responsible for the energy transfer between the vibrational modes;
• Model calculation of the anharmonic coupling constants;
• Anharmonic excitation rate of the hindered rotational phonons using Keldysh diagram technique;
• Pauli master equation approach to calculate the probability of rotations due to anharmonic decay of high frequency CH stretch mode;
• Keldysh-Green’s function derivation of the combination band two-phonon rotation excitation.

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I. DFT CALCULATION RESULTS

The DFT calculations were performed in SIESTA using a supercell of the Cu(001) with a 4x4 surface and 4 atoms thick slab. Calculational details include a real space cutoff of 200 Ry, Gamma points approximation, double/single-z polarized (DZP/SZP) basis set for the C (DZP), H(DZP), and Cu(SZP) atoms. Computational details for the vibrational frequencies, electron-phonon coupling, and electron-hole pair damping can be found in Ref. 2. For the nudged elastic band (NEB) calculation more refined computational parameters were necessary, a 5x5 surface, 600 Ry cutoff, 3x3 k-points, and the DZP basis set for all species. Using the refined parameters changed vibrational frequencies by less than 10 %. Although the NEB calculation is fairly converged with computational parameters, the calculated barrier is still approximate because of the basis set superposition error inherent in the SIESTA method. We therefore use the experimental barrier height in the main text.

The equilibrium configuration of C2H2 on Cu(001) and the relaxation of the Cu atoms is shown schematically in Fig. 1. The results for the vibrational energies $\hbar \Omega_\nu$, $\nu = 1, \ldots, 12$ are shown in Tab. I of the main text.

The calculated equilibrium configuration of the chemisorbed C2H2 molecule on Cu(001) in agreement with Ref. 1: $d_{CC} = 1.40 \text{ Å}, d_{CH} = 1.12 \text{ Å}$ and bond angle CC-H is 120.7°. The acetylene atom displacements for all modes are illustrated in Fig. 2 where only four Cu atoms nearest to the acetylene molecule are shown as blue balls.

I. DFT CALCULATION RESULTS

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The equilibrium configuration of C2H2 on Cu(001) and the relaxation of the Cu atoms is shown schematically in Fig. 1. The C-C and CH bond lengths and C-CH bond angle are given in the text.

II. ANHARMONIC COUPLING THE CH STRETCH MODES WITH OTHER VIBRATIONAL MODES OF THE ADSORBED ACETYLENE

In this section we explicitly describe the scheme to calculate the normal coordinates modes of a system (in our case the system involves the acetylene molecule and the surface of copper) and then the anharmonic couplings between them.

Shifting each atom from the equilibrium position $\{\vec{R}_i\}$ with a displacement vector $\{\delta \vec{r}_i\}$ and expanding the molecule potential energy $U(\{\delta \vec{r}_i\})$ in Taylor series

$$U(\{\delta \vec{r}_i\}) = U_0 + \frac{1}{2} \sum_{i,j} \sum_{\alpha \beta = 1}^{N} a_{ij}^{\alpha \beta} \delta r_i^\alpha \delta r_j^\beta + o(||\delta r||^2),$$

where $i,j$ denote the atomic indices, $\alpha, \beta$ are the Cartesian indices, $U_0$ is the potential energy of the molecule in the equilibrium state and coefficients $a_{ij}^{\alpha \beta}$ are the matrix elements of

FIG. 1. Calculated equilibrium configuration of C2H2 on Cu(001). The C-C and CH bond lengths and C-CH bond angle are given in the text.
In order to estimate the anharmonic couplings between different modes we expand the potential energy to the next order

\[
U(\{\delta r_i'\}) = U_0 + \frac{1}{2} \sum_{i,j}^N \sum_{\alpha,\beta=1}^3 a_{ij}^{\alpha\beta} \delta r_i^\alpha \delta r_j^\beta + \frac{1}{6} \sum_{i,j,k}^N \delta r_i^\alpha \delta r_j^\beta \delta r_k^\gamma + o\left(||\delta r||^3\right). \quad (6)
\]

After rotating to the basis of normal coordinates we obtain

\[
U(\{\delta \tilde{q}_m\}) = U_0 + \frac{1}{2} \sum_{m=1}^{3N} \omega_m^2 \delta \tilde{q}_m \delta \tilde{q}_m + \frac{1}{6} \sum_{m,m',m''=1}^{3N} K_{m,m',m''} \delta \tilde{q}_m \delta \tilde{q}_m \delta \tilde{q}_{m''} + o\left(||\delta \tilde{q}||^3\right). \quad (7)
\]

where \(\{\delta \tilde{q}_m\}\) is a set of normal coordinates which represents a solution of the secular equation \((5)\) and \(K^{(c)}\) is classical anharmonic coupling between the vibrational modes of the systems. The transformation from the original Cartesian coordinates to the normal coordinates basis has a form

\[
K_{m,m',m''} = \sum_{i,j,k}^N e_m^\alpha e_{m'}^\beta e_{m''}^\gamma \sqrt{m_i} \sqrt{m_j} \sqrt{m_k} \quad (8)
\]

where \(e_m^\alpha\) is the eigenvector coefficient between normal coordinate \(\delta q_m\) and the shift of \(i\)-th atom in \(\alpha\) direction \(\delta r_i^\alpha\) - \(\delta \tilde{q}_m = \sum_{i,\alpha} e_m^\alpha \delta r_i^\alpha\).

To quantize the vibrational modes, we introduce a dimensionless displacement vector \(\delta q_m\), so that \(\delta \tilde{q}_m = \delta q_m \sqrt{h/(2\omega_m)}\) and arrive from coordinates to operators in canonical way \(\delta q_m \to \delta \tilde{q}_m\). Then, creation \(b_m^\dagger\) and annihilation \(b_m\) operators of the corresponding mode can be introduced and the cubic term in Eq. (7) is transformed to

\[
H_{an} = \frac{1}{6} \sum_{m,m',m''=1}^{3N} K_{m,m',m''} \left(b_m^\dagger + b_m\right) \left(b_{m'}^\dagger + b_{m'}\right) \left(b_{m''}^\dagger + b_{m''}\right). \quad (9)
\]

where the anharmonic coefficient \(K_{m,m',m''}\) is connected with classical one \(K_{m,m',m''}\) via

\[
K_{m,m',m''} = K_{m,m',m''}^c h^{3/2} \left(2 \sqrt{2} \omega_m^2 \omega_{m'}^2 \omega_{m''}^2\right)^{-1}. \quad (10)
\]

### III. SPRINGS ON RODS: A SIMPLER MODEL OF ACETYLENE ON Cu(100)

In order to estimate the anharmonic couplings \(K_{m,m',m''}\) we introduce the simpler model potential \(U(\{r_i\})\) and imply the scheme discussed in Supplementary material.

We propose to describe the CH, CC and C-nearest neighbor Cu bonds by springs on rods (the latter to fix the central character of the forces):

\[
U_{spr}(r_i, r_j) = \frac{\omega_{ij}^2}{2} \left(\sqrt{||r_i - r_j||^2 - L_{ij}}\right)^2, \quad (10)
\]
where $\omega_{ij}$ and $L_{ij}$ are the parameters (see in Tab. II) chosen to reproduce the calculated by DFT set of eigenfrequencies. The comparison of the DFT calculated eigenenergies with that within the simpler model are given in Table III.

| Bonds      | C-C | C-H | C-Cu (nearest) | C-Cu (next-nearest) |
|------------|-----|-----|----------------|----------------------|
| $\omega$, meV | 159 | 370 | 70             | 25                   |
| $L$, Å     | 1.39| 1.04| 1.94           | 2.23                 |

Table III. Comparison between the vibrational eigenfrequencies $\hbar\omega$ (in meV), within the DFT calculations (top row) and the simpler model.

We calculate the anharmonic coefficients $K_{n,m,n'}$ and find the modes coupled effectively. Figure 3 of the main text shows the dependence of coefficients $K_{1,1,1}$ and $K_{2,2,0}$ on mode numbers $n$ and $m$. These coefficients indicate the most effective ways of decay of the symmetric CH stretch mode #1 and asymmetric CH stretch mode #2. These modes are known to be responsible for the high-energy threshold $\sim 360$ meV, they are excited directly by the tunneling electrons.

The symmetric CH stretch mode #1 decays most efficiently via excitation of a pair of equivalent phonons: #4 CH asymmetric in-plane bend or wag, #5 in-plane bend or scissor, #6 out-of-plane bend or asymmetric rotation, #7 cartwheel. Coupling of the symmetric CH stretch mode #1 with the asymmetric rotation mode #11 is ineffective since the corresponding anharmonic coefficient is 70 times smaller than that for a coupling with the pair of out-of-plane bend or asymmetric rotation mode #6.

The asymmetric CH stretch mode #2 decays most efficiently via excitation of a pair of non-equivalent phonons, e.g., the pair of the asymmetric rotation #6 and cartwheel mode #7.

This simple estimation of the anharmonic coefficient shows that the rotation of the acetylene molecule is initiated via excitation of the asymmetric rotation mode #6. There are two processes leading to the excitation of the reaction coordinate mode #6, the excitation of a pair of the asymmetric rotation phonons or the excitation of one asymmetric rotation phonon and one phonon of the cartwheel mode #7.

IV. DOUBLE EXCITATION OF HINDERED-ROTATION MODE

In this section we derive explicitly the excitation rate of the reaction coordinate mode. As we have shown in Supplementary material the excitation process of the vibrational mode of the acetylene molecule involves two possible pathways, via excitation of the reaction coordinate mode and the auxiliary idler mode or via double excitation of the reaction coordinate mode (terms $H_{ph,1}$ and $H_{ph,2}$ respectively, in Eq. (8) of the main text).

We discuss here both of the scenarios using the Keldysh diagram technique. In both cases, under consideration the frequencies of the vibrational modes are far from the resonance, $\Omega_h > 2\Omega_r \sim \Omega_r + \Omega_i$ and the anharmonic interaction between them can be treated as weak.

In what follows we derive the excitation rate of the RC mode due to the process described by $H_{ph,1}$: the excitation rate due to $H_{ph,2}$ can be obtained replacing the index $i$ of the idler phonon in all formulas below, with the index $r$ of the RC phonon.

For the description of the effective stationary occupation densities of the RC mode we use the kinetic equation. The anharmonic component of the excitation rate of the RC mode is given by the one-loop polarization operator. Neglecting the temperature corrections, it reads

$$\Gamma_{in}(\omega, \Omega_r, V) = \frac{2\pi}{h} |K_{h,i}^2| \int n_{ph}^{(i)}(\epsilon + \omega) \rho_{ph}^{(i)}(\epsilon + \omega) \left[ 1 + \rho_{ph}^{(i)}(\epsilon) \right] \rho_{ph}^{(i)}(\epsilon) d\epsilon, \quad (11)$$

where $\rho_{ph}^{(i)}(\epsilon)$ is the density of states of the RC and high-frequency modes and $n_{ph}^{(i)}(\epsilon)$ are the corresponding occupation densities. Formula (11) describes the energy transfer rate to the hindered rotation mode of an absorbate due to the anharmonic coupling with the CH stretch mode.

We proceed with the calculation of a total excitation rate $\Gamma_{i_{het}}(\Omega_r, V)$ of the RC mode

$$\Gamma_{i_{het}}(\Omega_r, V) = \int \Gamma_{in}(\omega, \Omega_r, V) \rho_{ph}^{(i)}(\omega) d\omega. \quad (12)$$

After making a substitution of (11) into (12) the total RC excitation rate takes the form

$$\Gamma_{i_{het}}(\Omega_r, V) \approx 2\pi |K_{h,i}^2| \rho_{ph}^{(i)}(\Omega_r + \Omega_i) \rho_{ph}^{(i)}(\Omega_r + \Omega_h)$$

$$+ 2\pi |K_{h,i}^2| \rho_{ph}^{(i)}(\Omega_h) \left[ \rho_{ph}^{(i)}(\Omega_h - \Omega_i) + \rho_{ph}^{(i)}(\Omega_h - \Omega_r) \right]. \quad (13)$$

The second term in Eq. (13) shows a threshold dependence on bias voltage, because it is proportional to the high-frequency mode occupation numbers $n_{ph}^{(i)}(\Omega_h) = \Gamma_{i_{het}}(\Omega_h)/2\gamma^{(i)}(\Omega_h)$. It can be shown that the first term in (13) can be omitted due to the fact that $n_{ph}^{(i)}(\Omega_h + \Omega_i) \ll n_{ph}^{(i)}(\Omega_h)$.

The total excitation rate of the RC phonons due to the anharmonic term $H_{ph,1}$ is then

$$\Gamma_{i_{het}}(\Omega_r, V) \approx 2\pi |K_{h,i}^2| \frac{\Gamma_{i_{het}}(\Omega_h)}{2\gamma^{(i)}(\Omega_h)} \left[ \rho_{ph}^{(i)}(\Omega_h - \Omega_i) + \rho_{ph}^{(i)}(\Omega_h - \Omega_r) \right], \quad (14)$$

and due to $H_{ph,2}$ is

$$\Gamma_{i_{het}}(\Omega_r, V) \approx 4\pi |K_{h,i}^2| \frac{\Gamma_{i_{het}}(\Omega_h)}{2\gamma^{(i)}(\Omega_h)} \rho_{ph}^{(i)}(\Omega_h - \Omega_i). \quad (15)$$

Note that both rates are proportional to the CH stretch mode excitation rate $\Gamma_{i_{het}}(\Omega_h)$ and to small phonon densities of the RC and idler vibrational modes far from the resonance.
V. LADDER CLIMBING WITH TWO- AND ONE-STEP PROCESSES

In this section we calculate the excitation rate of the RC phonons \( R_B(V) \) using Pauli master equations. As discussed in Supplement [14] depending on the height of the rotational barrier, two possible processes can lead to initiation of the rotations of the acetylene molecule on Cu(001). In this section these processes will be considered separately as they involve ladder climbing of two different types.

In case when the rotational barrier height is \( \Omega < \varepsilon_B < 2\Omega \), the one-step ladder climbing process takes place. The excitation rate of this process \( \Gamma_{\text{rot},1}(\Omega, V) \) is given by (14) and the relaxation rate is \( \gamma^{\text{rel}}_{\text{ch}} \), thus the Pauli master equation can be written as

\[
\frac{dP_m}{dt} = (m + 1)\gamma^{\text{rel}}_{\text{ch}} P_{m+1} + m\Gamma_{\text{rot},1}(\Omega, V)P_{m-1}
- [m\gamma^{\text{rel}}_{\text{ch}} + (m + 1)\Gamma_{\text{rot},1}(\Omega, V)]P_m. \tag{16}
\]

The stationary solutions (in respect to \( P_0 \)) for \( m = 1 \) states in the localization potential of the RC mode can be written as

\[
P_0 = 1, \quad P_1 = \Gamma_{\text{rot},1}(\Omega, V)(\gamma^{\text{rel}}_{\text{ch}})^{-1}P_0 \ll P_0.
\]

Reaction rate \( R_B(V) \) is defined as a probability rate to overcome the localization potential barrier and in our notations it is the excitation rate from the first excited level

\[
R_B^{(1)}(V) = 2\Gamma_{\text{rot},1}(\Omega, V)(\gamma^{\text{rel}}_{\text{ch}})^{-1} \tag{17}
\]

If the rotational barrier height is \( 2\Omega < \varepsilon_B < 3\Omega \) then the excitation rate is assumed to be dominated by the two-phonon anharmonic coupling with the high-frequency mode. The pair of RC phonons excitation rate \( \Gamma_{\text{rot},2}(\Omega, V) \) is given by (15) and the de-excitation process is dominated by the single phonon relaxation rate \( \gamma^{\text{rel}}_{\text{ch}} \). Then, according to Ref. [4], the Pauli master equation takes form

\[
\frac{dP_m}{dt} = (m + 1)\gamma^{\text{rel}}_{\text{ch}} P_{m+1} + m(m - 1)\Gamma_{\text{rot},2}(\Omega, V)P_{m-2}
- [m\gamma^{\text{rel}}_{\text{ch}} + (m + 2)(m + 1)\Gamma_{\text{rot},2}(\Omega, V)]P_m. \tag{18}
\]

The stationary solutions (in respect to \( P_0 \)) for \( m = 0, 1, 2 \) states in the localization potential of the RC mode can be written as

\[
P_0 = 1, \quad P_1 = 2\Gamma_{\text{rot},2}(\Omega, V)(\gamma^{\text{rel}}_{\text{ch}})^{-1}P_0 \ll P_0\text{ and }
P_2 = \frac{(\gamma^{\text{rel}}_{\text{ch}} + 6\Gamma_{\text{rot},2}(\Omega, V))}{2\gamma^{\text{rel}}_{\text{ch}}}P_1 \approx \frac{\Gamma_{\text{rot},2}(\Omega, V)}{\gamma^{\text{rel}}_{\text{ch}}}P_0. \tag{19}
\]

Reaction rate \( R_B(V) \) in this case is a sum of the excitation rates from the first excited state \( 6\Gamma_{\text{rot},2}(\Omega, V)P_1 \) and from the second excited state \( 12\Gamma_{\text{rot},2}(\Omega, V)P_2 \),

\[
R_B^{(2)}(V) = 24\Gamma_{\text{rot},2}(\Omega, V)(\gamma^{\text{rel}}_{\text{ch}})^{-1}. \tag{20}
\]

The reaction rate in both cases is a quadratic function of the RC phonon excitation rate which is a feature of the two-step ladder climbing process and differs only in a proportionality coefficient. For a more accurate estimation of proportionality coefficient between the second power inelastic tunneling current and rotation rate we need to take into account the fact that the inelastic tunneling current is a sum of several components which arise from the scattering of tunneling elections on all relevant vibrational modes. In our case we are interested in two CH stretch modes, symmetric #1 and asymmetric #2. According to our DFT calculation the inelastic transmission modes through these modes are \( T^{(1)} = 1.3 \times 10^{-11} \text{s}x\text{V}^{-1} \) and \( T^{(2)} = 5.9 \times 10^{11} \text{s}x\text{V}^{-1} \). In what follows we will take this into account. Introducing the probability factors to excite the symmetric CH stretch mode \( \zeta = T^{(1)}(T^{(1)} + T^{(2)}))^{-1} = 0.18 \) and the asymmetric one \( (1 - \zeta) = 0.82 \).

Substituting the expression for the excitation rate of the RC phonons (14) and (15) into Eqs. (17) and (20) correspondingly and using the expression for the high-frequency phonons \( \gamma^{(\Omega)}_{\text{ph}}(\Omega_h, V) = \Gamma_{\text{rot}}(\Omega_h, V) (2\gamma^{(\text{rel})}_{\text{ch}})^{-1} \) occupation densities we obtain the proportionality coefficient \( B^{(1)} \) [Eq. (9) of the main text] between the excitation reaction rate and the phonon generation rate \( R_B^{(1)}(V) = B^{(1)}\Gamma_{\text{rot},1}(\Omega_h, V) \).

\[
B^{(1)} = 2\pi^2K^2_{h,\text{rot}}(1 - \zeta)^2 \frac{1}{\Omega^{\gamma^{(\text{rel})}_{\text{ch}}} \gamma^{(\text{rel})}_{\text{ch}}}
(\rho^{(\Omega)}_{\text{ph}}(\Omega_h - \Omega_r) + \rho^{(\Omega)}_{\text{ph}}(\Omega_h - \Omega_r))^2. \tag{21}
\]

Using \( K_{h,\text{rot}} \approx 32 \text{ meV}, \gamma^{(\Omega)}_{\text{ph}} = 0.2 \text{ ps}^{-1}, \gamma^{(\text{rel})}_{\text{ch}} = 0.7 \text{ ps}^{-1}, \gamma_r = 0.7 \text{ ps}^{-1}, \Delta = \Omega_h - \Omega_r \approx 208 \text{ meV} (\Omega_h \approx \Omega_r) \) we obtain \( B^{(1)} \approx 3.5 \times 10^{-15} \text{s} \). It is 7 times larger than the coefficient \( B = 6 \times 10^{-16} \text{s} \) obtained from the best fit of the experimental data.

Moreover, in case of a lower reaction barrier \( \Omega < \varepsilon_B < 2\Omega \) the process of double excitation of the reaction coordinate phonons gives a contribution to the linear part \( \Gamma_{\text{rot}}(V) \) of the rotation probability. The rotation rate can be estimated then as \( R_{\text{rot}}(V) = \Gamma_{\text{rot}}(V) \). Then the impact of this process into the proportionality coefficient \( A \) can be written as

\[
A^{(2)} = 4\pi^2K^2_{h,\text{rot}}(1 - \zeta)^2 \left( \frac{\rho^{(\Omega)}_{\text{ph}}(\Omega_h - \Omega_r)}{\gamma^{(\text{rel})}_{\text{ch}}} \right)^2. \tag{22}
\]

Using the same parameters as above for the coefficient \( B^{(1)} \), we arrive to the estimated value of \( A^{(2)} = 6 \times 10^{-3} \), which is three orders of magnitude larger than the value of \( A \) obtained from the fitting of the experimental data. Evidently, this makes the case of a lower reaction coordinate barrier \( \Omega < \varepsilon_B < 2\Omega \) hardly possible.

Analogously, the coefficient \( B^{(2)} \) between \( R_B^{(2)}(V) \) and \( \Gamma_{\text{rot},2}(\Omega_h, V) \),

\[
B^{(2)} = 48\pi^2K^2_{h,\text{rot}}(1 - \zeta)^2 \left( \frac{\rho^{(\Omega)}_{\text{ph}}(\Omega_h - \Omega_r)}{\gamma^{(\text{rel})}_{\text{ch}}} \right)^2. \tag{23}
\]

Using \( K_{h,\text{rot}} \approx 32 \text{ meV}, \gamma^{(\Omega)}_{\text{ph}} = 1 \text{ ps}^{-1}, \gamma^{(\text{rel})}_{\text{ch}} = 0.7 \text{ ps}^{-1}, \Delta = \Omega_h - 2\Omega_r \approx 208 \text{ meV} \) we obtain that \( B^{(2)} \approx 2.4 \times 10^{-15} \text{s} \), 5 times larger than the best fit value \( B = 6 \times 10^{-16} \text{s} \).
Thus the estimated value of the coefficient $B$ is slightly larger than the value obtained from the fit of the experimental data. We believe that our simpler model overestimates the anharmonic coupling coefficients $|K_{h,r,r}|$; for a better agreement with the experimental data we have to take $\approx 1.5$ times smaller values $K_{h,r,r} \sim 20$ meV.

VI. COMBINATION BAND SINGLE ELECTRON PROCESS: KELDYSH TECHNIQUE FORMULATION

In this section we show that in the limit of a low temperature $T = 0$ the excitation rate of phonons excited simultaneously via tunneling electron scattering can be written in the same form as for the single-electron excitation.

In order to calculate an excitation rate of coherent phonons we use the Keldysh-Green’s function method. The kinetic equation for phonons takes the form

$$\frac{\partial N_{c,i}}{\partial t} = \int \left[ \Pi_{c,i}^+(\omega) D_{c,i}^-(\omega) - \Pi_{c,i}^-(\omega) D_{c,i}^+(\omega) \right] \frac{d\omega}{2\pi}, \quad (24)$$

where $i = 1, 2$; $N_{c,i}$ is a total number of phonons in corresponding mode. $D_{c,i}^\pm$ are phonon Keldysh-Green’s functions and $\Pi_{c,i}^\pm$ are phonon polarization operators. The former are given by

$$D_{c,i}^+(\omega) = -2i\pi \left( 1 + n_{ph}^{(c)}(\omega) \right) p_{ph}^{(c)}(\omega), \quad (25)$$

$$D_{c,i}^-(\omega) = -2i\pi n_{ph}^{(c)}(\omega) p_{ph}^{(c)}(\omega), \quad (26)$$

where $n_{ph}^{(c)}(\omega)$ is the vibration occupation function of $i$-th mode to be determined self-consistently from the kinetic equation.

Substituting $D_{c,i}^\pm(\omega)$ in the kinetic equation, we obtain

$$\frac{\partial N_{c,i}}{\partial t} = (i) \int d\omega p_{ph}^{(c)}(\omega) \left[ \Pi_{c,i}^+(\omega) - (\Pi_{c,i}^+(\omega) - \Pi_{c,i}^-(\omega)) n_{ph}^{(c)}(\omega) \right]. \quad (27)$$

At low temperatures, $k_BT \ll \Omega_{c,i}$ the occupation density takes the form $n_{ph}^{(c)}(\omega) \approx \Gamma_{in}(\omega,\Omega_{c,i}, V) \left( \gamma_{tot}^{(c)}(\omega) \right)^{-1}$, where

$$\Gamma_{in}(\omega,\Omega_{c,i}, V) \gamma_{tot}^{(c)}(\omega)$$

are the excitation and relaxation rates of the corresponding phonon modes. Then $\Gamma_{in}(\omega,\Omega_{c,i}, V) = \Pi_{c,i}^+(\omega)$.

The self-energy $\Pi_{c,i}^+(\omega)$, expanded to the second order in $\eta$ [see Eq. (10) of the main text] reads

$$\Gamma_{in}(\omega,\Omega_{c,i}, V) = \Pi_{c,i}^+(\omega) = -i\eta^2 \int \frac{d\omega'}{2\pi} \frac{d\omega}{2\pi} D_{c,i}^+(\omega') G_a^{(+)}(\omega') G_a^{(+)}(\omega - \omega'), \quad (28)$$

where $G_a(\epsilon)$ are the Keldysh-Green’s functions of the electrons of the adsorbate. Substituting $D_{c,i}^+(\omega')$ and taking into account that $n_{ph}^{(c)}(\omega) \ll 1$, we arrive to the following expressions for the polarization operators

$$\Gamma_{in}(\omega,\Omega_{c,i}, V) = \eta^2 \int \frac{d\omega}{2\pi} G_a^{(+)}(\omega) G_a^{(+)}(\epsilon - \omega - \Omega_{c,2}), \quad (29)$$

In full analogy we obtain the expression for $\Gamma_{in}(\omega,\Omega_{c,2}, V)$. Total coherent phonon excitation rate $\Gamma_{coh} = \Gamma_{coh}(\Omega_{c,1}, V) = \Gamma_{coh}(\Omega_{c,2}, V) \equiv \int \Gamma_{in}(\omega,\Omega_{c,i}, V) p_{ph}^{(c)}(\omega) d\omega$ takes the same form for both modes

$$\Gamma_{coh} = 2\pi \eta^2 \int G_a^{(+)}(\epsilon - \Omega_{c,1} - \Omega_{c,2}) G_a^{(+)}(\epsilon) d\omega. \quad (30)$$

The expression in a limit $T = 0$ and $\Delta_s \ll \Delta_s$ can be approximated as

$$\Gamma_{coh}(V) \approx \gamma_{coh}(\Omega_{c,1} + \Omega_{c,2}) \frac{\Delta_t}{\Delta_s} F(\Omega_{c,1} + \Omega_{c,2}, eV), \quad (31)$$

where $F(\Omega, eV) = (eV - \Omega \theta ([eV] - \Omega)$ and $\gamma_{coh}(\omega) = 2\pi \eta^2 \rho_{ph}^2(\epsilon_F) \omega$ is the relaxation rate of the coherent phonons. We can use the inverse lifetime of the coherent modes $\gamma_{coh}^{(c,1)}$ and $\gamma_{coh}^{(c,2)}$ and rewrite $\Gamma_{coh}(V) = K_{coh} \Gamma_{coh}(\Omega_{c,1} + \Omega_{c,2}, V)$, where

$$\Gamma_{coh}(\Omega_{c,1} + \Omega_{c,2}, V) = \frac{\gamma_{coh}^{(c,1)} + \gamma_{coh}^{(c,2)}}{\Omega_{c,1} + \Omega_{c,2}} \frac{\Delta_t}{\Delta_s} F(\Omega_{c,1} + \Omega_{c,2}, eV), \quad (32)$$

and $K_{coh} = \gamma_{coh}^{(c,1)} + \gamma_{coh}^{(c,2)}$ is the efficiency of the coherent process.

Equation (32) shows that the total coherent phonon excitation rate takes the form of a single-phonon excitation rate $\Gamma_{coh}(\Omega, V)$, where the single vibrational frequency is replaced by the sum of two vibrational frequencies.

1 S. G. Tikhodeev and H. Ueba, Phys. Rev. B 70, 125414 (2004)
2 S. W. Gao, Surf. Sci. 313, 448 (1994).
3 L. V. Keldysh, Zh. Eksp. Teor. Fiz. 20, 1018–1030 (1965).