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Quantum-state-resolved reactivity of overtone excited CH₄ on Ni(111): Comparing experiment and theory

P. Morten Hundt,¹ Maarten E. van Reijzen,¹ Rainer D. Beck,¹ Han Guo,² and Bret Jackson²
¹Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
²Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, USA

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Quantum state resolved reactivity measurements probe the role of vibrational symmetry on the vibrational activation of the dissociative chemisorption of CH₄ on Ni(111). IR-IR double resonance excitation in a molecular beam was used to prepare CH₄ in three different vibrational symmetry components, A₁, E, and F₂, of the 2ν₃ antisymmetric stretch overtone vibration as well as in the ν₁ + ν₃ symmetric plus antisymmetric C–H stretch combination band of F₂ symmetry. The quantum state specific dissociation probability S₀ (sticking coefficient) was measured for each of the four vibrational states by detecting chemisorbed carbon on Ni(111) as the product of CH₄ dissociation by Auger electron spectroscopy. We observe strong mode specificity, where S₀ for the most reactive state ν₁ + ν₃ is an order of magnitude higher than for the least reactive, more energetic 2ν₃-E state.

Our first principles quantum scattering calculations show that as molecules in the ν₁ state approach the surface, the vibrational amplitude becomes localized on the reacting C–H bond, making them very reactive. This behavior results from the weakening of the reacting C–H bond as the molecule approaches the surface, decoupling its motion from the three non-reacting C–H stretches. Similarly, we find that overtone normal mode states with more ν₁ character are more reactive: S₀(2ν₁) > S₀(ν₁ + ν₃) > S₀(2ν₃). The 2ν₃ eigenstates excited in the experiment can be written as linear combinations of these normal mode states. The highly reactive 2ν₁ and ν₁ + ν₃ normal modes, being of A₁ and F₂ symmetry, can contribute to the 2ν₃-A₁ and 2ν₃-F₂ eigenstates, respectively, boosting their reactivity over the E component, which contains no ν₁ character due to symmetry. Published by AIP Publishing.

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I. INTRODUCTION

The dissociative chemisorption of methane on transition metal surfaces has been studied in great detail both experimentally and by theoretical methods due to its importance in the steam reforming process used by the chemical industry to convert natural gas and water into synthesis gas.¹,² Methane dissociation on Ni(111) occurs by a direct mechanism where the incident molecules either dissociate on impact to form CH₃(ads) + H(ads) or scatter non-reactively back into the gas phase. Early molecular beam experiments have shown that methane dissociation can be activated both by incident translational energy and vibrational excitation of the incident molecule.³⁴ Quantum state resolved reactivity measurements using laser preparation of different vibrational modes of the methane clearly show that the dissociation is mode specific³ and bond selective.⁵,⁶ Alignment of the incident methane molecules by polarized laser radiation uncovered steric effects in methane dissociation.⁷,⁸ To date, state resolved reactivity data for the dissociation of CH₄ on Ni(111) and Ni(100) have been published¹⁰–¹² for the states ν = 0, ν₃, ν₁, ν₂ + ν₄, 2ν₃-F₂, and 3ν₄.

We have recently introduced state preparation by double resonance excitation¹³ for state resolved sticking coefficient measurements of CH₄ prepared in overtone and combination vibrations, including states that cannot be prepared by single photon excitation from the vibrational ground state due to symmetry restrictions. Here, we report the first results of state resolved reactivity measurements on Ni(111) for CH₄ prepared in the states ν₁ + ν₃, 2ν₃-F₂, 2ν₃-A₁, and 2ν₃-E. In Sec. II we briefly describe our experimental methods and in Sec. III we report our findings. Surprisingly, for these four eigenstates, as the vibrational energy increases the dissociative sticking probability decreases. In addition, the difference in reaction probability between the lowest energy and highest energy state can be quite large: roughly an order of magnitude. First, we examine this behavior using simple models that describe to what extent the vibrational amplitude for these states can localize on a single C–H stretch. We then compare the experimental data to the predictions of first principles quantum dynamical calculations, using a potential energy surface based on DFT (Density Functional Theory). The theory reproduces both the rough magnitude and overall reactivity trends observed in the experiments, and provides additional understanding of the origins of the observed behavior. We conclude with a brief summary in Sec. IV.

II. EXPERIMENTAL

The C–H stretching overtone vibrations of CH₄ include 2ν₁, ν₁ + ν₃, and 2ν₃, where 2ν₁ is the nondegenerate (A₁) overtone of ν₁, the symmetric C–H stretch normal mode, ν₁ + ν₃ the combination vibration of symmetric and antisymmetric C–H stretch, and 2ν₃ the overtone of the triply degenerate (F₂) antisymmetric C–H stretch normal mode ν₃. While the 2ν₃ overtone vibration is sixfold degenerate in the harmonic
approximation, it splits due to anharmonicity into three vibrational components with $A_3$, $E$, and $F_2$ symmetry in the $T_d$ group. Of these, only the $F_2$ component is accessible by direct single photon overtone excitation from the $v = 0$ ground state of $A_1$ symmetry. However, using IR-IR double resonance excitation with two infrared photons, it is possible to prepare CH$_4$(2$\nu_1$) in all three vibrational symmetry components$^{14,15}$ and prepare the effect of these nearly isoenergetic vibrations on the dissociative chemisorption probabilities of CH$_4$ on a clean Ni(111) surface. A simplified level-diagram of the excitation path is shown in Figure 1.

The molecular beam/surface science apparatus, the state specific reactant preparation by rapid adiabatic passage (RAP), and the product detection by AES have been described in previous publications.$^{16,17}$ Briefly, a continuous molecular beam of methane was generated by expanding pure CH$_4$ or 3% CH$_4$ seeded in helium with a backing pressure of 2 bar through a temperature controlled nozzle of 30 $\mu$m diameter. A 1 mm diameter nickel skimmer was used to extract a molecular beam from the supersonic expansion. The speed distribution of the molecular beam for different seed ratios and nozzle temperatures was measured by time-of-flight techniques with an on-axis quadrupole mass-spectrometer (QMS) and a chopper-wheel. Table I shows the average kinetic energy $E_0 = 1/2mv_0^2$ and the translational temperature $T_{\text{trans}}$ of CH$_4$ in the molecular beam obtained by fitting a flux weighted Maxwell Boltzmann speed distribution $f(v)$ to the TOF data,

$$f(v) = v^3 \exp \left[ \frac{m}{2kT_{\text{trans}}} (v - v_0)^2 \right].$$

<table>
<thead>
<tr>
<th>CH$_4$ seed ratio (%)</th>
<th>$T_s$ (K)</th>
<th>$E_0$ (kJ/mol)</th>
<th>$T_{\text{trans}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>305</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td>3 in He</td>
<td>300</td>
<td>23</td>
<td>7</td>
</tr>
<tr>
<td>3 in He</td>
<td>473</td>
<td>37</td>
<td>23</td>
</tr>
</tbody>
</table>

Two independently tunable continuous wave infrared optical parametric oscillators (OPO-1 and OPO-2, Argos Aculight) were used for state specific preparation of overtone excited CH$_4$ by double resonance excitation. The OPO idler frequencies were stabilized by locking them to sequential rotational transitions ($v=1 \leftarrow v=0$ to $v=2 \leftarrow v=1$) of CH$_4$ using Doppler-free absorption features detected in static gas cells. OPO-1 was locked to a Lamb dip of the P(0) $v_3$ fundamental transition of CH$_4$ at 3009.0114 cm$^{-1}$ detected in the Doppler-broadened absorption line using a static gas cell at room temperature.$^{18}$ The 3.4 W idler output of OPO-1 traversed a second gas cell of 90 cm length filled with 150 $\mu$bar of CH$_4$ where it selectively pumps population from $v = 0$, $J = 1$ to $v_3 = 1$, $J = 0$ only for molecules moving perpendicular to the IR beam. The Doppler-free population created by OPO-1 was probed by overlapping the pump and probe IR beams in the gas cell and scanning OPO-2 over the R(0), $v_3 = 2 \leftarrow 1$ transition. OPO-2 was then frequency locked to the peak of the Doppler-free absorption signal for R(0), $v_3 = 2 \leftarrow 1$ transition with a FWHM of 3.5 MHz.

The idler outputs of OPO-1 and OPO-2 were focused by cylindrical lenses ($f = 25.4$ cm) to intersect the molecular beam at two locations separated by 30 mm to excite CH$_4$ in an IR-IR double resonance scheme by rapid adiabatic passage 25 mm from the Ni(111) surface. Details of the RAP excitation have been described earlier.$^{16}$ A pyroelectric detector could be moved into the molecular beam past the excitation region to detect and quantify the flux of vibrationally excited molecules in order to verify that complete population inversion was achieved in both excitation steps.

III. RESULTS AND DISCUSSION

A. Experiment: State resolved reactivity measurements

State resolved reactive sticking coefficients of CH$_4$ prepared in four different C–H stretch overtone eigenstates were measured on the Ni(111) surface held at surface temperature $T_s = 475$ K. The nascent dissociation products of the incident CH$_4$ are a chemisorbed methyl group, CH$_3$(ads), and a hydrogen atom H(ads). At $T_s = 475$ K, CH$_3$(ads) rapidly dehydrogenates to form C(ads) and H(ads). The hydrogen atoms leave the Ni(111) surface by associative desorption to form H$_2$(g). Following a deposition experiment, the surface coverage of C(ads) was measured locally by Auger electron energy spectroscopy (AES) by scanning the sample surface in front of a commercial cylindrical mirror analyzer AES system (Omicron AES-150). Figure 2 shows a typical AES trace obtained by performing line scans across the 10 mm diameter Ni(111)
The vibrational energy of the eigenstates. Preparation of CH4 in the \( v_1 + v_3 \) eigenstate with the lowest vibrational energy of 5851 cm\(^{-1}\) results in nearly an order of magnitude higher reactivity than in the highest energy state 2\( v_3 \)-E state at 6054 cm\(^{-1}\). \( S_0(2\nu_3-A_1) \) and \( S_0(2\nu_3-F_2) \) are the same within the experimental error and fall in between the reactivity range spanned by \( S_0(v_1 + v_3) \) and \( S_0(2\nu_3)-E \). At the highest translational energy studied (37 kJ/mol), the difference between the state resolved reactivities decreases while the ordering stays the same.

The fact that the reactivity of the four different C–H stretch overtone states does not scale with their rovibrational energy excludes a prediction of the reaction rate by statistical theories.\(^{19,20}\) Rather, the ordering of the CH4 reactivity of the four overtone states may be rationalized by considering the differences in localization of the C–H stretch amplitudes for these states. Abram et al.\(^{21}\) analyzed the C–H stretch overtone states of CH4 using anharmonic symmetrized internal coordinates (SIC), expanding the vibrational states in a local mode basis. One can put 2 quanta of energy in a single C–H stretch 4 ways, denoted \( |2000;A_1 \rangle \), \( |0200;A_1 \rangle \), \( |0020;A_1 \rangle \), and \( |0002;A_1 \rangle \). The corresponding SIC states are orthonormal linear combinations of these states that transform like the irreducible representations of the T\(_d\) point group. We get one symmetric combination of \( A_1 \) symmetry and three antisymmetric combinations of \( F_2 \) symmetry, denoted \( |2000;A_1 \rangle \) and \( |2000;F_2 \rangle \), respectively. Similarly, there are 6 ways to put one quantum of energy each into two different C–H stretches; \( |1100 \rangle \), \( |1010 \rangle \), etc. These can be combined into delocalized SIC modes of \( A_1 \), \( E \), and \( F_2 \) symmetry, denoted \( |1100;A_1 \rangle \) and \( |1000;F_2 \rangle \), respectively. In Table II we list the percent contributions to the C–H stretch overtone states using this SIC basis set. We see that the C–H stretch amplitude is most strongly localized in a single C–H bond for the \( v_1 + v_3 \) eigenstate, followed by \( 2v_1 \), then the \( 2v_3-A_1 \) and \( 2v_3-F_2 \)-symmetry states, while for the \( 2v_3-E \)-symmetry state the C–H amplitude is completely delocalized and contains only \( |1100 \rangle \) character. The stronger localization of the C–H stretch amplitude in a single C–H bond for the vibrations of \( A_1 \) and \( F_2 \)-symmetry is consistent with the higher reactivity of these states compared to the \( E \)-state with its delocalized vibrational amplitude. In addition, given the anharmonicity of the C–H stretch, the \( |2000 \rangle \) states are lower in energy than the \( |1100 \rangle \) states, and increased \( |2000 \rangle \) character results in a lower energy for the \( 2v_3 \)-symmetry states. The result is the observed anti-correlation between vibrational energy and reactivity for the three \( 2v_3 \) overtone states.

This behavior is analogous to the mode specificity observed\(^5\) for the dissociation of CH2D2 on Ni(100) where the \( |20 \rangle \) local mode state (two quanta of C–H stretch excitation localized in a single C–H bond) has been measured for dissociation.
to be as much as five times more reactive than the delocalized (111) state (one quantum of C–H stretch in each of the two C–H bonds). DFT calculations of the transition state (TS) structure for methane dissociation on Pt and Ni surfaces predict that the dissociating C–H bond is significantly stretched (r_c–H = 1.49 Å for the TS on Pt(111) compared to 1.09 Å for the gas phase). Localizing the C–H stretch amplitude in a single C–H bond via excitation of a state with l20 character makes the reactant resemble the transition state more than excitation of a (111) state which distributes the C–H amplitude over two C–H bonds, one of which becomes a spectator in the dissociation. Jiang and Guo expressed this idea of deforming the reactant towards the transition state structure in a quantitative way by proposing a sudden vector projection (SVP) model. The SVP model calculates the projection of the reactant vibrational state (vector) onto the transition state structure and establishes a correlation between the magnitude of the SVP value for a given vibrational state and the promotional effect of this state on the reactivity. Unfortunately, the SVP model cannot be applied to overtone states. In addition, as a sudden model, the SVP approach neglects intramolecular vibrational redistribution (IVR) that can occur during the approach of the reaction partners.

Even if the initial vibrational state does not already localize the C–H stretch amplitude in a favorable way for the reaction, surface induced IVR may still lead to such a localization and can therefore be responsible for vibrational mode specific reactivity in a gas/surface reaction. This is consistent with the experimentally observed and mode specificity between the v1 and the v3 mode of CHx. Here, the four dimensional vibrationally adiabatic model described by Halonen et al. predicts that the totally symmetric A1 normal mode v1 evolves adiabatically to a localized excitation in a single C–H bond pointing towards the surface. On the other hand, the initially prepared antisymmetric F2-v3 normal mode becomes localized on the CH3 moiety pointing away from the surface. Based on this difference in C–H stretch localization, Halonen et al. predict that exciting the v1 mode will increase the dissociation probability more than the nearly isonenergetic v3 mode.

The SIC formulation provides a very satisfying picture, but it clearly has limitations. We see, for example, in Fig. 3 that the reactivities of the 2v3-A1 and -F2 states are about the same, while in Table II the A1 component has 4 times the |2000 state of the 2v3-A1 component as the F2 component. Also, as noted, molecules excited to the v1 state can be more reactive than those excited to the v3 state, even though the SIC representations of these two states differ only in the relative phases of the C–H vibrations. Another complication is that anharmonicity mixes the normal mode states. In Table III we show the results of a 4th order perturbative calculation by Wang and Sibert, who computed the vibrational eigenstates of methane using a dressed normal mode basis set with an accurate ab initio quartic force field. From now on, to distinguish between the true vibrational eigenstates and their normal mode components, we will include the symmetry label when we refer to the eigenstate, as we have already done with 2v3-E, etc. Thus, in Table III, the 2v1-A1 eigenstate is comprised of 74% of the 2v1 normal mode, 13% of the 2v3 normal mode, and so on. Note the bend character of the eigenstates: v2 is the doubly degenerate bend and v4 is the triply degenerate bend. As the frequencies of the stretch modes are about twice that of the bending modes, the 2-quantum stretch states mix with 1-quantum stretch plus 2-quantum bend states such as v1 + 2v2 and v2 + v1 + v4, and even some 4-quantum bend states (not shown). It is interesting to revisit our analysis based on the SIC states, given this mixing. For example, we can compute the percentage of |2000 (local mode character in the 2v1-F2 state as 0.73(11%) + 0.15(88%) = 21%. Similarly, we find 0%, 28%, 43% and 47% 2000 character for the 2v3-E, 2v3-A1, v1 + v3-F2, and 2v1-A1 states, respectively. This is a bit more consistent with experiment than the earlier analysis, as it now suggests that the F2 and A1 components of 2v3 have similar reactivities.

However, these reactions are clearly more complicated than can be explained by a model that includes only C–H stretching motions. Not only do bending types of motion contribute significantly to the states excited in the experiment, we see in Table III that the dissociative sticking probability actually increase as the amount of bending character increases. The excited state with the largest S0 in our experiments, v1 + v3-F2, is comprised of only 54% 2-quanta stretch normal modes, with the next largest contribution (29%) coming from the 4-quantum bend 3v2 + v4. Clearly, bending types of motion are very important as demonstrated by state resolved reactivity measurements for methane dissociation on Pt(110) where the vibrational efficacy of stretch-bend combination states was observed to be higher than for both pure stretch overtones and bend overtone states.

### B. Theory: Reaction path Hamiltonian (RPH) model for methane dissociation

Jackson and co-workers have developed a first-principles model for CH4 dissociation based on a minimum energy reaction path calculated by DFT. We only briefly review this model here, as details can be found in several recent publications. The DFT-based Vienna ab initio simulation package (VASP), developed at the Institut für Materialphysik of the Universität Wien, is used to compute total energies. The interactions between the ionic cores and the electrons are described by fully nonlocal optimized projector augmented-wave (PAW) potentials, and we use the Perdew-Burke-Ernzerhof (PBE) function and treat exchange-correlation effects. The Ni(111) surface is modeled as a series of infinite slabs separated by large vacuum space, using a 4-layer 3 × 3 supercell with periodic boundary conditions. To generate our full-dimensional potential energy surface we first locate the minimum energy path (MEP) for reaction, and compute the total energy V0(s)
at several dozen points along this path. The distance along the path in mass-weighted coordinates is $s$. At each of these points, we compute and diagonalize the force-projected Hessian to find the 14 normal vibrational coordinates $Q_k$ and corresponding frequencies $\omega_k(s)$ describing motion orthogonal to the reaction path in the harmonic approximation. Ignoring any higher order anharmonic terms, our potential can be written as follows:

$$V = V_0(s) + \sum_{k=1}^{14} \frac{1}{2} \omega_k^2(s) Q_k^2. \quad (1)$$

In Fig. 4, we plot $h\omega_k(s)$ along the reaction path for CH$_4$ chemisorption on Ni(111). When methane is far above the surface there are nine bending and stretching normal modes with nonzero frequency. The remaining five modes correspond to rotational and translational motion at large negative $s$. At the transition state ($s = 0$), the carbon atom is roughly over the top site and the reacting C–H bond is angled towards the metal, with the other three C–H bonds angled away. The MEP is symmetric with respect to reflection through a plane perpendicular to the surface and including the reacting bond. We label the 9 normal modes comprising the bends and stretches as $1'–6'$ and $1''–3''$ to indicate whether they are symmetric ($A'$) or antisymmetric ($A''$) with respect to this reflection.

We write the total molecular wave function as follows:

$$\Psi(t) = \sum_n \chi_n(s;t) \prod_k \phi_n(Q_k;s), \quad (2)$$

where the $\phi_n$ are harmonic oscillator eigenfunctions that depend parametrically on $s$, because $\omega_k(s)$ varies along the reaction path. The corresponding eigenvalues are $h\omega_k(s)\{n_k + \frac{1}{2}\}$, and the vector $n$ labels the vibrational state corresponding to the set of quantum numbers $\{n_k\}$. The coupled equations of motion for the wave packets, $\chi_n(s;t)$, are of the form

$$i\hbar \frac{\partial \chi_n(s;t)}{\partial t} = \left[ \frac{1}{2}P_0^2 + V_0(s) + \sum_{k=1}^{14} h\omega_k(s)\{n_k + \frac{1}{2}\} \right] \chi_n(s;t) + \sum_{n'} F_{nn'} \chi_{n'}(s;t). \quad (3)$$

The wave packets thus evolve on vibrationally adiabatic potential energy surfaces corresponding to each vibrational state $n$, and the operators $F_{nn'}$ couple states of the same symmetry ($A'$ or $A''$). The $F_{nn'}$ are proportional to the vibrationally nonadiabatic couplings, computed using the eigenvectors from the diagonalization of the Hessians along the reaction path.

The sums over $n$ in Eqs. (2) and (3) include the vibrationally adiabatic ground state and all states with one or two vibrational quanta excited. Detailed expressions for the equations of motion and the coupling terms can be found in a recent publication. For a given initial vibrational state, $n_0$, standard techniques are used to evolve the wave packets and to energy-analyze the reactive flux. The result is the rigid-lattice reaction probability, $P_0(E_i, n_0)$. The five normal modes that have small frequencies when the molecule is far above the surface describe molecular translation parallel to the surface and rotation away from the MEP. Unlike the internal stretch and bend vibrations included in the $\Phi_n$, these other types of motion are not well described by a harmonic model, and must be treated differently. These five modes do not couple strongly to the internal bends and stretches in the entrance channel. The location of the molecular center of mass over the unit cell, $X$ and $Y$, changes little along the MEP in the entrance channel, with the carbon atom remaining more-or-less over the minimum barrier site. The rotation of the molecule in the entrance channel also follows the MEP. Thus, $P_0$ corresponds to reaction at the minimum barrier site only, with rotational motion treated adiabatically.

To compute the dissociative sticking probability $S_0$, we average $P_0$ over all other surface impact sites, correct the rotational treatment, and include the effects of lattice motion. At the relatively low collision energies of the experiment, reaction is only possible close to the MEP, and we use the following approximation to average over paths corresponding to impacts near the lowest barrier sites. Motion along $X$ and $Y$ is slow on collision time scales, given the relatively large molecular mass and our normal incidence conditions. Assuming that there is no steering of the incident methane along $X$ and $Y$, we average $P_0$ over all impact sites in the surface unit cell, using the following approximation to estimate $P_0$ for impact at a site $(X, Y)$ away from the minimum barrier site:

$$P_0(E_i, n_0; X, Y) \approx P_0(E_i - \Delta V, n_0). \quad (4)$$

$\Delta V(X, Y)$ is the increase in barrier height at $(X, Y)$ relative to the minimum barrier site, which we can approximate using the normal modes, or compute directly using DFT. Recent AIMD studies confirm this sudden behavior for $X$ and $Y$. These same studies suggest that the rotational behavior might be closer to sudden at high collision energies, while it should be closer to adiabatic at lower incident energies. We use an approach similar to Eq. (4) to estimate $S_0$ in the sudden limit, and define our final $S_0$ as a linear combination of these two limits, such that the behavior is adiabatic at lower incident energies and sudden at higher incident energies. Finally, to introduce the effects of lattice motion for a surface temperature $T$, we average $P_0$ over all displacements and momenta normal to the surface of the Ni atom over which methane dissociates. The momentum of this atom determines the relative collision velocity, and the displacements can
significantly change the barrier height. We use a Debye model to describe the motion of this Ni atom.29

In Fig. 5 we plot the computed dissociative sticking probabilities \( S_0 \) for the ground and several excited states of \( \text{CH}_4 \). Note that these are the harmonic normal mode eigenstates. For the ground state, we show both the rotationally sudden and adiabatic limits. The difference is roughly a factor of 4 in the sticking. For the excited states, we find that \( S_0(E_{v_1}) > S_0(E_{v_2v_3}) \). While this behavior has been observed experimentally on Ni(100)\(^{11,25} \) and reproduced by our RPH-based model,\(^{26} \) no data exist for \( S_0(E_{v_1}) \) on Ni(111). As noted, the vibrationally adiabatic model of Halonen et al. predicts that as \( \text{CH}_4 \) moves towards the surface the vibrational motion becomes localized on the reacting C–H stretch for molecules excited to the \( v_1 \) state, while for molecules in the \( v_3 \) state it localizes on the non-reacting methyl group.\(^{26} \) Thus, molecules excited to the \( v_1 \) state are likely to be more reactive. We see the same behavior in our model, corresponding to the strong mode softening of the \( v_1 = 3' \) mode in Fig. 4. As the molecule approaches the transition state, the reacting C–H bond weakens, its frequency decreases, and it decouples from the relatively unperturbed higher-frequency C–H stretches in the non-reacting methyl group. This is the origin of the vibrational localization observed in the model of Halonen et al. However, our model also includes the non-adiabatic coupling between these states, and this turns out to be extremely important. In the adiabatic limit (\( F_{\text{nu}} = 0 \) in Eq. (3)) each wave packet remains on the vibrationally adiabatic potential energy surface corresponding to its vibrational state. Because of mode softening, the barrier along the vibrationally adiabatic reaction path for the \( v_1 \) state is lowered to 0.70 eV, while for the \( v_3 \) state it is about 0.87 eV (an average of the \( 1' \), \( 2' \) and \( 1'' \) components), similar to the vibrational ground state. While the barrier for reaction is significantly lower along the \( v_1 \) adiabatic path, this only partly explains the mode specificity, as much of the data in Fig. 5 are for energies below these barriers. At these low energies, the mechanism for reaction involves vibrationally non-adiabatic transitions between states, though lattice motion effects can also be very important. For example, a molecule initially in the \( 3' \) state can jump to the \( 4' \) state at the avoided crossing, and then to the \( 5' \) state, and so on. As the wave packet transitions to vibrational states of lower energy, the excess energy is converted to motion along the reaction path, increasing the reaction probability. In addition, the modes exchange character at the crossings, preserving the localization of vibrational energy on the reactive C–H bond. We find a strong non-adiabatic coupling at all the avoided crossings of Fig. 3,\(^{29} \) as well as between the \( 2' \) and \( 3' \) modes far above the surface where they are nearly degenerate (peaking near \( s = -5 \)). This surface induced IVR is responsible for much of the behavior observed in the experiments. Molecules excited to either the \( 2' \) or \( 3' \) mode exhibit similar behavior, as these modes mix in the entrance channel. The \( 1' \) mode couples only weakly to the \( 2' \) or \( 3' \), and the \( 1'' \) does not couple to the \( A' \) modes at all due to symmetry. Thus, we predict that Ni(111) molecules in the \( v_1 \) (\( 3' \)) state are two to three times more reactive than molecules in the \( v_3 \) (\( 1' \), \( 2' \), \( 1'' \)) state. Note that a purely vibrationally adiabatic model predicts that molecules in the \( v_3 \) state are about as reactive as those in the ground state. In fact, experiment, like our theory, finds a strong vibrational enhancement;\(^{35,46,47} \) the \( v_1 \) enhancement is simply larger.

These same ideas explain the behavior of the two-quanta stretch overtones. Due to the \( 3' \) mode softening the (average) vibrationally adiabatic barriers for the \( 2v_1 \), \( v_1 + v_3 \), and \( 2v_3 \) states are 0.52, 0.69, and 0.86 eV, respectively. We see in Fig. 5 that sticking follows this trend, \( S_0(E_{v_1}, 2v_1) > S_0(E_{v_1}, v_1 + v_3) > S_0(E_{v_3}, 2v_3) \), and mode softening certainly contributes to this behavior at higher energies. At energies below these barrier heights, however, lattice motion and non-adiabatic transitions are responsible for reaction. The preferred reaction path is \( 3' \) to \( 4' \) to \( 5' \) and so on, and the \( 2v_1 (=3' + 3') \) state is thus the most reactive, followed by \( v_1 + v_3 \). The components of \( v_1 + v_3 \) and \( 2v_3 \) that contain \( 2' \), such as \( 3' + 2' \) and \( 2' + 2' \), respectively, are more reactive than those containing \( 1' \) and \( 1'' \), because surface induced IVR mixes \( 2' \) with \( 3' \).

This is also consistent with much of the experimental data in Fig. 3. We see that molecules in the \( v_1 + v_3 \) state are more reactive than those in one of the \( 2v_3 \) components. In addition, looking at Table III, the most reactive symmetry components of \( 2v_3 \), are those containing \( 2v_1 \) and \( v_1 + v_3 \) character. However, we can take this a bit further by actually propagating the true (mixed) eigenstates computed by Wang and Sibert\(^{27} \) (see Table III). Using our reaction path approach, it is possible to write an initial state of the form \( c_a |v_a⟩ + c_b |v_b⟩ \), where \( |v_a⟩ \) and \( |v_b⟩ \) are two harmonic normal modes, propagate the total wave function, and compute \( S_0 \). However, we have found that this gives the same result as simply averaging the normal mode sticking probabilities; i.e., \( c_a^2 S_0(v_a) + c_b^2 S_0(v_b) \). We take the latter approach here.

A minor problem is that we are not able to directly calculate sticking probabilities for initial vibrational states that contain three or more quanta, and these contribute to some of the eigenstates excited in the experiments (see Table III). However, we can reasonably estimate \( S_0 \) for these states by examining how the \( S_0 \) vs. \( E_i \) curves shift with vibrational excitation. In Fig. 6 we see that the computed \( S_0 \) curve for the \( v_2 \) state is shifted about 0.11 eV from the \( S_0 \) curve for the ground state. The curve shifts about 0.10 eV from the \( v_2 \) state to the \( 2v_3 \) state, which is slightly smaller as the total molecular energy.

![Graph showing dissociative sticking probability of CH4 on Ni(111) vs incident energy E_i for the molecule in the ground state (gs), vibrationally excited (v), or vibrationally excited and excited (gs-sud). Theoretical curves for \( v_1 \), \( v_1 + v_3 \), and \( 2v_3 \) components are also plotted.](image-url)
is getting closer to the barrier height. If we add a quantum of \( \nu_2 \) bend to the higher energy \( \nu_1 \) state, we thus expect to see an even smaller shift, and indeed the \( S_0 \) curve shifts about 0.07 eV from the \( \nu_1 + \nu_2 \) state to the \( \nu_1 + \nu_3 + \nu_4 \), giving the curve in Fig. 6. Although this approach is arbitrary, the errors in the estimated energy shifts are likely to be small. In addition, as we will show, the overall reactivity is dominated by contributions from the \( \nu_2 \), \( \nu_1 + \nu_3 \), and \( \nu_2 \) normal mode components.

In Fig. 7 we plot the results of our calculations and compare with the experimental data from Fig. 3. Overall, the calculations reproduce the experimental trends, if not always the magnitude of the sticking. \( 2\nu_3 \)-E is the least reactive symmetry component, giving approximately the same \( S_0 \) as the normal mode \( 2\nu_3 \) state, as it comprised almost entirely of this state (94%). The \( 2\nu_3 \)-A and \( 2\nu_3 \)-F symmetry components have contributions from the more reactive \( 2\nu_1 \) and \( \nu_3 + \nu_1 \) normal mode states, making them more reactive than the \( 2\nu_3 \)-E state, with \( S_0(2\nu_3 \text{-} A_1) \) a bit larger than \( S_0(2\nu_3 \text{-} F_2) \) in both theory and experiment. The \( \nu_1 + \nu_3 \)-F state is more reactive than any component of the \( 2\nu_3 \) state, for the reasons discussed, but the difference is smaller than that observed in the experiments. At the highest energy of the experiments the theory reproduces both the ordering and the magnitude of the measured sticking probabilities quite well. At the lowest energy, the computed \( S_0 \) is too small by almost a factor of two for the \( 2\nu_3 \)-A and \( 2\nu_3 \)-F symmetry components and almost a factor of three for the \( \nu_1 + \nu_3 \) state. Thus, for these three states the experimentally measured efficacies for promoting a reaction become bigger, relative to that for the \( 2\nu_3 \text{-} E \) state, as the incident energy becomes very small. We note that similar behavior was found for the \( 2\nu_3 \) symmetry states of CH\(_4\) for dissociation on Ni(111). Our RPH-based calculation does not reproduce this change in the relative efficacy with energy, and the theory curves in Fig. 7 maintain roughly the same spacing at all energies considered. The origin of this behavior is not clear, though at these low energies the sticking probabilities can be very sensitive to the presence of defects. It is possible that the vibrational efficacies could be different on, say, step edges, than on the terrace sites.

Finally, it is interesting to note that the bend-plus-stretch combinations of Fig. 6 are reasonably efficacious for promoting dissociation. We find that, for example, at \( E_t = 0.1 \) eV, \( S_0 \) for the 1-stretch plus 2-bend combinations (\( \nu_3 + 2\nu_4 \), \( \nu_2 + \nu_3 + \nu_4 \), etc.) are all about the same, and only slightly smaller than \( S_0(2\nu_3) \). However, at this energy, \( S_0(\nu_1 + \nu_3) \) is three times larger and \( S_0(2\nu_1) \) is almost five times larger. As a result the \( 2\nu_3 \), \( \nu_1 + \nu_3 \), and \( 2\nu_1 \) normal mode components dominate the overall reactivity of the states excited in the experiment. In the end, symmetry and the unique reactivity of the 3′ mode control the ordering in Fig. 3. Due to the latter, \( S_0(2\nu_1) > S_0(\nu_1 + \nu_3) > S_0(2\nu_3) \). The \( 2\nu_1 \) and \( \nu_1 + \nu_3 \) normal modes, being of \( A_1 \) and \( F_2 \) symmetry, can contribute to the \( 2\nu_3 \text{-} A_1 \) and \( 2\nu_3 \text{-} F_2 \) eigenstates, respectively, boosting their reactivity over the \( E \) component, which contains no \( \nu_1 \) character due to its symmetry.

IV. SUMMARY

In summary, we have measured the state resolved dissociation probability of CH\(_4\) on Ni(111) at \( T_s = 475 \) K for four different C–H stretch overtone states using double resonance excitation of the reactants and Auger detection of dissociation products. We propose that the observed mode specificity is due to differences in the degree of C–H stretch amplitude localization at the transition state for the different initially prepared states. We compare the state-resolved reactivity data obtained from our experiments with the results of quantum scattering calculations using a DFT-based potential energy surface. These calculations show that all the normal vibrational modes of CH\(_4\), the symmetric stretch, \( \nu_1 \), has the largest efficacy for promoting a reaction. This is a result of the weakening of the reacting C–H bond as the molecule approaches the transition state. The corresponding drop in vibrational frequency causes this C–H stretch to decouple from the three nonreacting C–H stretches. Thus, as the molecule approaches the surface, one of the 4 C–H stretch normal modes will decrease in
frequency, and the vibrational amplitude will become localized on the reacting C–H bond. This particular mode adiabatically correlates with the $\nu_1$ stretch, making molecules excited to this state unusually reactive. Vibrationally nonadiabatic transitions to lower states preserve this behavior and allow for reactions at energies below the vibrationally adiabatic barrier height. For these reasons, we find that overtone states with more $\nu_1$ character are more reactive, and $S_0(2\nu_1) > S_0(\nu_1 + \nu_3) > S_0(2\nu_3)$. The $2\nu_3$ eigenstates excited in the experiment are split into three symmetry components due to anharmonicity, and each component contains contributions from these normal mode states, as well as various stretch plus two-bend normal mode states. The highly reactive $2\nu_1$ and $\nu_1 + \nu_3$ normal modes, being of $A_1$ and $F_2$ symmetry, can contribute to the $2\nu_3$-$A_1$ and $2\nu_3$-$F_2$ eigenstates respectively, boosting their reactivity over the E component, which contains no $\nu_1$ character due to its symmetry.

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