SUPPLEMENTARY MATERIAL:

I. Fitting of the Hessian matrix

In the fitting of the Hessian matrix elements as functions of the reaction coordinate, one can take advantage of symmetry. The non-diagonal elements may be written in the form of numerical derivatives as

$$H(\alpha,\beta) = \frac{E(\Delta\alpha,\Delta\beta) - E(\Delta\alpha,-\Delta\beta) - E(-\Delta\alpha,\Delta\beta) + E(-\Delta\alpha,-\Delta\beta)}{4\delta^2}.$$
 (S1)

Here, α and β label any of the 15 atomic coordinates in {C_x, C_y, ..., H4_z}, $E(\Delta \alpha, \Delta \beta)$ denotes the DFT energy of CH₄ interacting with Ni(111) with a small displacement along α and β , and δ the small displacement used in the second order differencing. For example, the $H(C_x, C_y)$ (or $H(C_y, C_x)$) is 0, since $E(\Delta C_x, \Delta C_y) = E(\Delta C_x, -\Delta C_y)$ and $E(-\Delta C_x, \Delta C_y) = E(-\Delta C_x, -\Delta C_y)$.

From Eq.S1, one can deduce the symmetry properties of *H* of methane interacting with Ni(111) in a geometry belonging to the C_s symmetry (Fig. 1 in the paper): (1) there are always 18 zero elements in the lower triangle of the Hessian matrix (see Fig. S1), (2) the main block matrices A, B and F (see Fig. S1) can be split up in six 3×3 sub-blocks, namely A₁, A₂, B₁, B₂, F₁ and F₂, in which the absolute values of all the corresponding elements in the sub-blocks corresponding to each other are numerically identical to each other except for the sign of their off-diagonal elements, (3) the triangular matrices E₁ and E₂ are also numerically the same except for the sign of their off-diagonal terms, (4) the

block D is a unique block and its off-diagonal terms differ only from each other in their sign. The symmetry properties (2) and (3) may also be described as follows: let X be A, or B, or C, or E, or F. We then have for (i, j = 1, 2, 3):

$$X_{ii}^{1} = X_{ii}^{2} , (S2)$$

$$X_{ij}^{1} = -X_{ij}^{2}, (S3)$$

The symmetry property (4) can be described by

$$D_{ij} = -D_{ji}.$$
 (S4)



Figure S1: The schematic Hessian matrix for methane interacting with Ni(111) in a geometry with C_S symmetry. The 18 zeros are displayed in the lower triangle in addition with the sub-block matrices of A, D, B and F and the two triangular blocks of E_1 and E_2 . The sub blocks of these main blocks are separated by a line.

As stated before, the numerical noise in the forces obtained from the plane wave code may alter the symmetry properties of *H*. To obtain a correct C_s symmetrized *H*, we first fitted the components of the force (gradient components) to functions of ρ , employing 13 model functions listed in Table S1. In each case, we simply selected the function providing the best fit by calculating the average absolute deviation. In the second step, we obtained noise reduced Hessian matrix elements using a second order numerical differencing of the force components. The obtained H was then symmetrized using

$$\hat{H}_{ij} = \hat{H}_{ji} = \frac{H_{ij} + H_{ji}}{2}.$$
(S5)

The additional symmetry conditions discussed above were imposed by inserting zeros in the places illustrated in Fig. S1. We also applied *'numerical padding'* to the sub-blocks. This was achieved by: (1) averaging the sub-blocks in A, B, E and F matrices by,

$$\hat{X}_{ij}^{\ 1} = \hat{X}_{ij}^{\ 2} = \frac{|X_{ij}^{\ 1}| + |X_{ij}^{\ 2}|}{2},$$
(S6)

followed by the mapping the signs of X_{ij}^{1} onto X_{ij}^{1} and then applying Eq. S3 to the offdiagonal elements of X_{ij}^{2} , (2) symmetrizing the D block using,

$$\hat{D}_{ij} = \frac{|D_{ij}| + |D_{ji}|}{2}$$
(S7)

and applying,

$$\hat{D}_{ij} = -\hat{D}_{ji} \,. \tag{S8}$$

Table S1: The table shows the 13 model functions used in the fitting of the forcecomponents. The a_i are the coefficients of the model functions. x denotes the reaction coordinate.

1.	a_1+a_2x
2.	$a_1+a_2x+a_3x^2$
3.	$a_1 + a_2 x^2$
4.	$a_1 + a_2 x^3$
5.	$a_1 + a_2 x + a_3 x^2 + a_4 x^3 + a_5 x^4$
6.	$a_1 + a_2 x + a_3 x^2 + a_4 x^3 + a_5 x^4 + a_6 x^3$
7.	$a_1 + a_2 / x$
8.	a_1/x
9.	$a_1 + a_2/x + a_3/x^2$
10	$a_1 + a_2/x + a_3/x^2 + a_4/x^3$
11	$a_1x + a_2/x^2 + a_3/x^3$
12	$a_1(\sin(x)\cos(x)/x) + a_2\sin(x) + a_3\cos(x) + a_4x$
13	$a_1sin(x) + a_2cos(x)$

II. Approximation of the vibrational wavefunction by normal modes

In this section we justify the use of normal modes instead of the vibrational wave function for the Massey velocity calculations by stating the close correspondence of the *inner product* in the quantum function and classical normal eigenvector spaces. This close correspondence is based on the quantum eigenfunction being a ' \hbar -deformation' of the classical normal mode solution.

The classical and quantum mechanical solutions of a harmonic oscillator resemble each other in several ways. Although for the system considered (CH₄ interacting with a rigid Ni(111) surface) the classical solution – the normal modes – lies on a limited 15dimensional Hilbert space (since it is defined in an \mathbb{R}^n space with n=15), it shows many one-to-one correspondences with its quantum counterpart (the vibrational eigenfunction) such as unique vibrational eigenvalues and having similar spatial-properties such as orthogonality, completeness, norm, Schwarz inequality (or in general, the Gram determinants¹) etc. Furthermore, the *inner product* in both the quantum function and classical normal mode eigenvector spaces are defined in the space of L^2 (i.e. Lebesgue space with 2-norm), which is a square-integrable (or square-summable) linear space². In quantum eigenfunction space the *projection* of a vibrational eigenfunction at ρ_i on another eigenfunction at ρ_j is evaluated as the overlap integral, whereas it corresponds to the dot product of the corresponding normal mode coefficients in the classical case .

In addition to this, a proof exists of the correspondence between the classical eigenvector and vibrational quantum eigenfunction³. This is based on the ' \hbar -

deformation' of the classical eigenvector. The proof of this deformation does not depend on the number of particles or the potential and assumes that the quantum eigenfunctions are *square integrable* over \mathbf{R}^{n} .

Following the above arguments, one can write the relation between the vibrational eigenfunction, Ψ , of a harmonic oscillator and the corresponding normal mode eigenvector, *F*, as

$$\lim_{\hbar \to 0} \Psi = F , \tag{S9}$$

where $F = \sum_{i} f_{i} x_{i}$, f_{i} are the components of *F* with respect to the Cartesian atomic coordinates x_{i} .

Similarly another vibrational quantum eigenfunction, Φ corresponding to a different normal mode eigenvector, G can be written as,

$$\lim_{\hbar \to 0} \Phi = G , \tag{S10}$$

where $G = \sum_{i} g_{i} x_{i}$ and g_{i} are the vector components of the normal mode G.

Then the correspondence between the overlap integral of Ψ and Φ and the dot product of the *F* and *G* is related by,

$$\lim_{\hbar \to 0} \langle \Psi | \Phi \rangle = \sum_{i} f_{i} g_{i} = \langle F | G \rangle.$$
(S11)

References:

- 1. Methods of Mathematical Physics, Vol. 1, by R. Courant and D. Hilbert, Interscience publishers, inc., New York, (7/e), pgs. 34, 62 (1966).
- 2. Real Analysis: Measure Theory, Integration, and Hilbert Spaces, *by E. M. Stein and R. Shakarchi, Princeton University Press*, pg. 157 (2004).
- 3. I. Loris and R. Sasaki, *Physics Letters A*, 327, 152 (2004).