Supporting Information

Mode-Specific Chemisorption of CH_4 on Pt{110}-(1×2) Explored by First-Principles Molecular Dynamics

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Appendix I

The symmetrised internal coordinates described in Section 3.3 do not provide a perfectly accurate representation of the normal modes of the isolated methane molecule because the ν_3 and ν_4 modes, belonging to the T_2 representation, cannot be described as neither pure stretching or bending modes, but are instead a combination of bond elongations (S_{3x}, S_{3y}, S_{3z}) and angular deformations (S_{4x}, S_{4y}, S_{4z}). Symmetrised coordinates have the advantage of being represented by simple linear combinations of either bond elongations or angle deformations, but, even in the simple quadratic force-field approximation, the use of this set of coordinates implies the presence of cross terms (with the associated force constant F_{34}) in the expression describing the quadratic potential:[1]

$$2V = F_{11}S_1^2 + F_{22}(S_{2a}^2 + S_{2b}^2) + F_{33}(S_{3x}^2 + S_{3y}^2 + S_{3z}^2) + F_{44}(S_{4x}^2 + S_{4y}^2 + S_{4z}^2) + 2F_{34}(S_{3x}S_{4x} + S_{3y}S_{4y} + S_{3z}S_{4z})$$

In this study, we have transformed the symmetrised S coordinates (eq 1) into normal mode coordinates by diagonalization of the force constant matrix associated with nuclear motion along S_3 and S_4.[1] Since the off-diagonal terms in the force constant matrix are relatively small, only a minor correction to the expression of S_3 and S_4 coordinates is needed to transform them into genuine normal mode coordinates (Q): $Q_{3i} = aS_{3i} + bS_{4i}$ and $Q_{4i} = aS_{4i} + bS_{3i}$, where i = x, y, z (a = 0.997595, b = 0.069318), while the normal mode coordinates for ν_1 and ν_2 are unchanged ($Q_1 = S_1, Q_2 = S_2$).

The vibrational force constants (F_{11}, F_{22}, F_{33}, F_{34} and F_{44}) associated with each mode have been calculated from the vibrational frequencies obtained by normal mode analysis for the isolated methane molecule, following the procedure described by Jones and Goldblatt.[2] Transformation into normal coordinates eliminates the cross term F_{34} and the remaining force constants have the values indicated in Table S1.

Table S1. Force constants associated with CH_4 normal modes (J/m^2).

$F(\nu_1)$	5.34083×10^2
$F(\nu_2)$	0.44139×10^2
$F(\nu_3)$	5.40695×10^2
$F(\nu_4)$	0.39237×10^2

REFERENCES

(1) Raynes, W. T.; Lazzeretti, P.; Zanasi, R.; Sadlej, A. J.; Fowler, P. W. *Molecular Physics* **1987**, *60*, 509 - 525.

(2) Jones, L. H.; Goldblatt, M. *Journal Of Molecular Spectroscopy* **1958**, *2*, 103-112.