Supporting Online Material

Materials and Methods

The experiments are performed in a triply differentially pumped supersonic molecular beam-surface scattering apparatus. Gas mixtures of CH_4 (99.99%) in H_2 (99.9999%) or He (99.9999%) expand into vacuum continuously through a 35 μm diameter nozzle source. Variations in nozzle temperature (298 – 830K) and seed ratio (2 and 5% in H_2, 2 and 5% in He, and 100% CH_4) produce supersonic molecular beams with CH_4 translational energies ranging from 9.2 to 139 kJ/mol and $\Delta E/E \leq 7\%$. Infrared light (3-4 mW) from a single mode, continuous wave color center laser ($\Delta\nu<1MHz$) crosses the molecular beam in the second differential pumping chamber and excites 10-20% of the methane molecules to v=1, J=2 of ν_3 via the R(1) transition at 3038.4985 cm^{-1}. The narrow linewidth of the laser and the sharp absorption profile of CH_4 molecules in the molecular beam allow us to excite a single rotational level of ν_3. A pyroelectric bolometer in the third differential pumping stage verifies and quantifies infrared absorption in the beam, and a computer-controlled servo system locks the laser frequency to the methane absorption transition of interest. The $100\mu s$ flight time from the optical excitation region to the surface is short relative to the radiative lifetime of the vibrationally excited state, so essentially all excited molecules impinge on the surface in their prepared state. A Ni single crystal polished to within 0.1° of the (111) plane is housed in an ultrahigh vacuum chamber (base pressure 6×10^{-11} Torr) and prepared using standard methods. Auger Electron Spectroscopy (AES) verifies surface cleanliness.

We quantify reactivity by exposing the surface to a molecular beam of CH_4 for a pre-selected time. The surface is held at 475 K during the beam dose to promote rapid recombinative desorption of any H_2 carrier gas that adsorbs to the surface.(1) The nascent products of CH_4 dissociation on Ni(111) are chemisorbed H and CH_3. At 475 K, CH_3 promptly dehydrogenates to C(ad) + 3 H(ad), H(ad) recombinatively desorbs, and chemisorbed C remains to signify a reactive scattering event.(2) After the dose is complete, AES quantifies the areal density of

chemisorbed C resulting from methane dissociation. A separate measurement quantifies the methane flux incident on the surface. Since the experiments are performed in the limit of low coverage (typically $\theta < 0.08$ ML), the ratio of the areal density of C atom reaction products (as determined by AES) to the incident flux (integrated over dose time) yields S_0. Control experiments verify that the C we detect arises from CH_4 dissociation and not from impurities in the beam gases or background contaminants in the ultrahigh vacuum chamber.

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2. Q. Y. Yang, K. J. Maynard, A. D. Johnson, S. T. Ceyer, *J. Chem. Phys.* **102**, 7734-7749 (1995).