

Calculations for methane scattering from Pt(111)

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Calculations are presented and compared with recently available experimental data for the scattering of CH₄ from a clean, ordered Pt(111) surface. The theoretical model was used earlier for describing data from the same laboratory for the scattering of CH₄ by LiF(001). The results are in good agreement with experiment for both the energy-resolved and total-intensity angular distribution spectra.

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Recently, data for the scattering of molecular beams of CH₄ by a clean, ordered Pt(111) surface have become available.¹⁻⁶ The purpose of this Brief Communication is to analyze and discuss these data in terms of a theoretical model that was successful in describing similar data taken at the same laboratory for the scattering of CH₄ from the insulator LiF(001).⁷

The CH₄/Pt(111) data consist of angular distributions which produce total scattered intensities for a given incident beam, and time-of-flight (TOF) energy-resolved spectra taken for fixed incident and final beam angles. The experimental apparatus is constrained to a fixed angle of 90° between the beam incident at the angle θ_i and the final detector direction θ_f , thus for the measured angular distributions each final angle corresponds to a different incident angle according to the relation $\theta_f = 90^\circ - \theta_i$. The energy resolution of the incident beam was $\Delta E/E = 0.06$ and the angular dispersion was less than 0.5° .²

Pt(111) is highly reactive and over a period of time under bombardment by the CH₄ beam the surface becomes contaminated with adsorbed molecules as well as dissociation products. In the experiment careful studies were made to assess the rate of build-up of contaminant products on the surface⁴ and it was found that for initial periods of several minutes after routine cleaning protocols were completed, the surface remained clean and the quality of the scattered spectra did not degrade. Thus all measurements considered here are for scattering from a clean and uncontaminated surface.

The theoretical model is a mixed classical-quantum description of the collision in which translational and rotational motion of the molecule and energy exchange to the surface phonons are treated classically and excitations of internal vibrational modes are treated with a semiclassical quantum theory.^{8,9} This model has also been used to explain the surface temperature and incident energy dependence of scattered angular distributions of C₂H₂ from LiF(001) (Ref. 10) and O₂ beams from the Al(111) surface.¹¹ Rotational and vibrational excitation of the CH₄ molecules are included in the theoretical calculations presented here, however, the experimental apparatus was not capable of measuring the internal state of the molecular projectiles. Neither the small energy resolution nor the angular dispersion of the

experimental incident beam has an appreciable affect the rather broad energy-resolved spectra calculated here, and this has been verified by trial calculations in which the results for a well-defined beam are convoluted with a Gaussian distribution of incident energies.

It is shown that both the angular distributions and the energy-resolved spectra for the CH₄/Pt(111) system can quantitatively be explained by the theoretical model. The results of the analysis give an estimate of about 40 meV for the physisorption well depth of the interaction potential for this system.

The differential reflection coefficient is obtained for classical conditions on the translational and rotational motion of the molecular projectile. This implies hypersonic translational energies, large masses compared to that of hydrogen and high rotational quantum numbers. The internal vibrational frequencies of CH₄ are large compared to the translational and rotational energies expected in these experiments and must be treated quantum mechanically. In this limit the differential reflection coefficient for a single collision with the surface can be written as an analytical expression, and the details are given in Ref. 7.

Phonon correlations at small distances on a smooth surface give rise to the two constants v_R and ω_R appearing in the differential reflection coefficients. v_R is a weighted average of phonon velocities parallel to the surface, whose value should be of the order or smaller than the Rayleigh mode speed^{12,13} and its value is chosen as 1700 m/s in all of the calculations shown here. ω_R is a weighted average frequency of the surface-parallel motions of librations of the substrate molecules.⁹ However, in the present calculations the value of ω_R is not an adjustable parameter because its value is chosen to be 10^{10} s^{-1} which is too small to produce any measurable effect. The physisorption potential is modeled by a square well of depth D and the crystal mass of the substrate is taken to be that of a single Pt atom.

The incident molecular beam in the experiments considered here is prepared in a state that approximates an equilibrium distribution of rotational and vibrational states at low temperatures. For the calculations we have averaged the incident beam over a Boltzmann distribution of rotational states at a temperature of 30 K, approximately the estimated

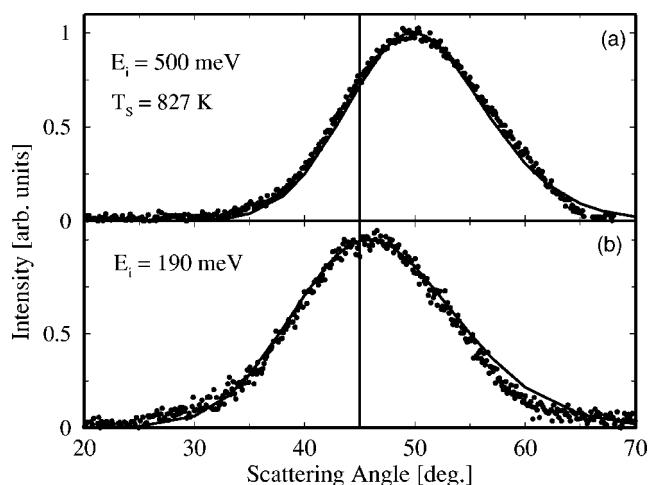


FIG. 1. Angular intensity distributions for methane CH_4 scattered from a Pt(111) surface compared to the calculations shown as solid curves. The incident translational energies are (a) 500 meV, (b) 190 meV. The surface temperature is 827 K. The vertical line marks the specular position.

experimental conditions. The vibrational temperature is estimated to be significantly less than 100 K and for the calculations presented here a value of 10 K was used. The calculations are essentially unchanged by variations of more than a factor of two in either of these parameters. The calculated results are averaged over angular orientation of the molecules, and over angular orientation of the angular momentum. The detector used in these experiments is a velocity-dependent density detector, and consequently the calculated spectra must be corrected by a factor of $1/p_f$ in order to compare with the measurements.

The calculations require the polarization vectors for the normal modes of the CH_4 molecule. These were obtained using a standard classical normal modes analysis in the harmonic approximation.^{7,14-16} For CH_4 there are a total of nine normal modes that have four distinct frequencies, three of which are degenerate. Calculations indicate that only the two lowest frequency modes with energies $\hbar\omega=190.2$ and 161.9 meV are appreciably excited under the experimental conditions considered here, with the maximum excitation probability at $E_i=500$ meV of approximately 4 and 5 %, respectively.

Angular distributions for the $\text{CH}_4/\text{Pt}(111)$ system were measured at two incident energies, $E_i=190$ and 500 meV, and for surface temperatures ranging from 400 to somewhat over 800 K. The crystal azimuthal direction was $\langle 11\bar{2} \rangle$. Figure 1 shows the experimental data compared to calculations for an angular distribution taken at a temperature of 827 K. The calculated curve is obtained by integrating the differential reflection coefficient over all final energies and final angular momenta, averaging over an initial Boltzmann rotational distribution at a temperature of 30 K, summing over all excitations of internal vibrational modes, and averaging over molecular orientations. The well depth is taken to be $D=40$ meV and the crystal mass M_C is that of a single Pt atom.

It is seen that the most probable angle of the angular distributions are slightly supraspecular at the lower incident

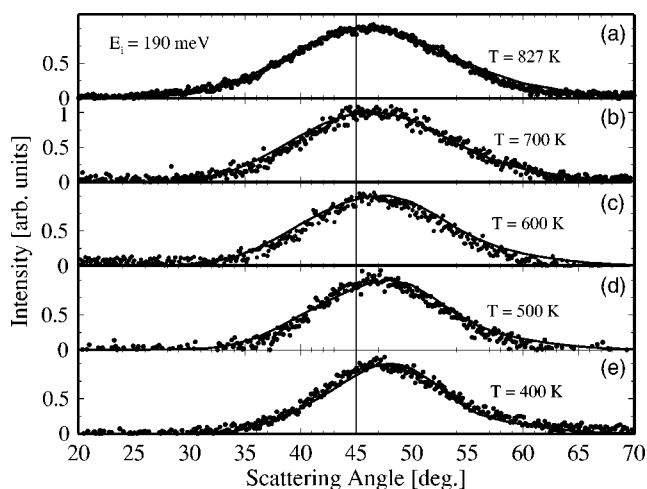


FIG. 2. Angular intensity distributions for different surface temperatures $T=827$ (a), 700 (b), 600 (c), 500 (d), and 400 K (e) as marked. The incident energy is 190 meV and the vertical line marks the specular position.

energy and approximately 5° larger than the specular position at the higher energy. The specular position $\theta_S=45^\circ$ is indicated by the vertical line. The experimental data and in particular the supraspecular shift with increasing energy are well described by the calculations. In addition the small decrease in full width at half maximum (FWHM) with the larger energy is matched by the calculations.

The temperature dependence of the angular distributions is shown in Fig. 2 which gives a series of graphs at the lower incident translational energy of 190 meV ranging from $T=400$ to 700 K. Also shown is the data at $T=827$ K from Fig. 1 which was taken on a different day. All other conditions are the same as in Fig. 1. It is seen that with increasing temperature there is a small subspecular shift of the most probable scattering angle toward the specular position and an increase in the full width at half maximum, both of which are well matched by the calculations. A similar subspecular shift with increasing temperature was observed previously in the $\text{CH}_4/\text{LiF}(001)$ measurements and also for the case of $\text{O}_2/\text{Al}(111)$ (Ref. 11) as well as for the case of rare gas scattering from metals.¹⁷

Time-of-flight energy-resolved spectra are shown in Fig. 3 for the same two energies and temperature as in Fig. 1. The incident beam and detector angles are both 45° . The calculations shown as solid curves are with a well depth of $D=40$ meV. The TOF time corresponding to elastic scattering is indicated by the vertical dashed line. The TOF time for recoil energy loss in a hard-sphere collision with a single Pt atom is indicated by the dash-dotted vertical line which at this specular scattering angle is about 15% of the incident energy. It is seen that under these scattering conditions the measured most probable final energy shows an energy loss of approximately the same as the expected recoil loss with a single surface atom, but there is a significant fraction of scattered CH_4 molecules that leave the surface at energies larger than that of the incident beam. The FWHM of the scattered distribution becomes significantly smaller with increasing incident energy. It is seen that the calculated curves match the

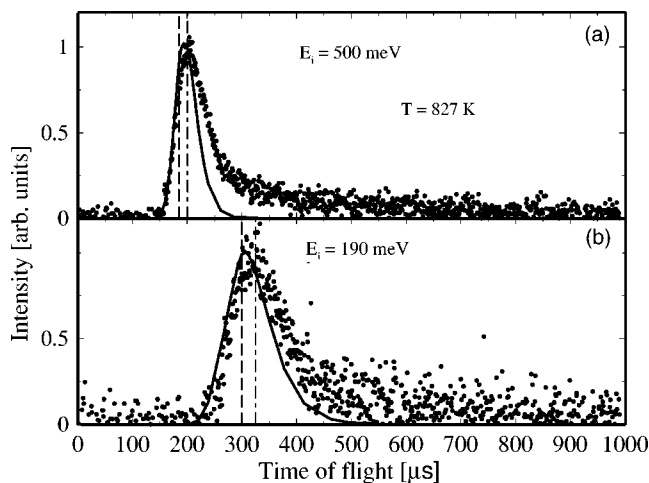


FIG. 3. Time-of-flight spectra of CH_4 molecules scattered from a Pt(111) surface for different translational energies 500 meV (a) and 190 meV (b). The incident angle is $\theta_i = 45^\circ$ and the surface temperature is 827 K. The two vertical lines indicate recoil energy loss (dashed-dotted line) and elastic scattering (dashed line).

peak position and the high energy (small TOF time) of the data, but do not explain the long tail at low energies. This low-energy tail may be the result of trapping and subsequent desorption which is not included in the calculations.

The temperature dependence of the TOF spectra is given in Fig. 4. Four different spectra at temperatures ranging from 400 to 700 K are shown for the same conditions as in Fig. 3, although these data were taken on different days and under somewhat different incident beam properties as indicated by the larger scatter in the data. It is clear that with increasing surface temperature the scattered distribution shifts to higher energies (smaller TOF times), i.e., the average energy loss is somewhat larger than 15% of the incident energy at the

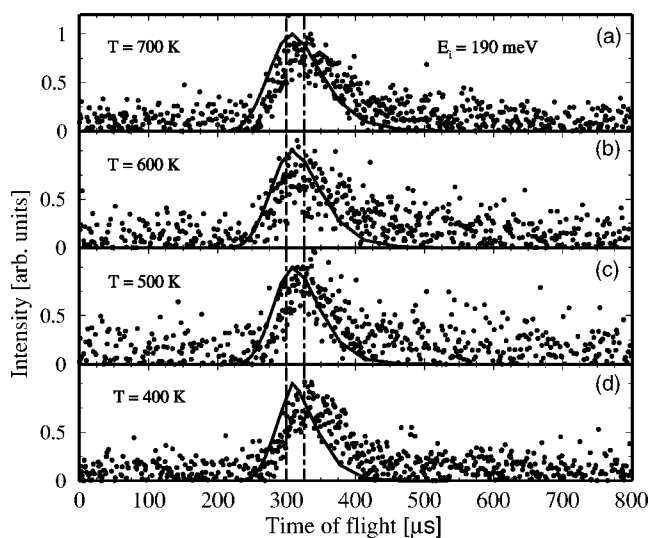


FIG. 4. Time-of-flight spectra for $\text{CH}_4/\text{Pt}(111)$ for different values of surface temperature T : 700 K (a), 600 K (b), 500 K (c), and 400 K (d). The incident angle $\theta_i = 45^\circ$ and the incident translational energy is 190 meV.

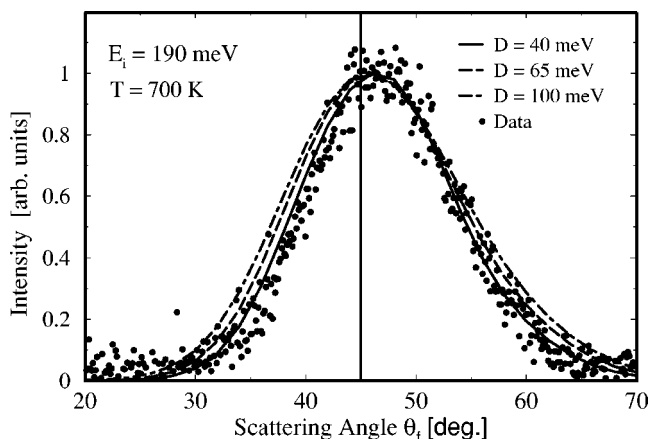


FIG. 5. Angular distributions for different values of the well depth D . The incident energy is 190 meV and the temperature is 700 K.

lowest temperature and slightly less than 15% at the largest temperature. The FWHM becomes broader with increasing temperature.

Comparison of the theoretical model to the experimental data provides an opportunity to obtain estimates of physical parameters such as the physisorption well depth of the interaction potential. Figures 5 and 6 show calculations at several well depths compared with data for both the angular distributions and the TOF spectra. The data is for the incident translational energy of 190 meV and the well depths are 40, 65, and 100 meV. For the higher incident energy of 500 meV, a small physisorption well gives virtually no change in the calculations.

From Fig. 5 it is evident that the effect of the physisorption well is to broaden the angular distribution particularly on the side of the peak nearest to normal. Clearly a small well with $D = 40$ meV gives the best fit for the angular distributions, and this holds true for calculations carried out at all measured temperatures. For the case of the TOF data the

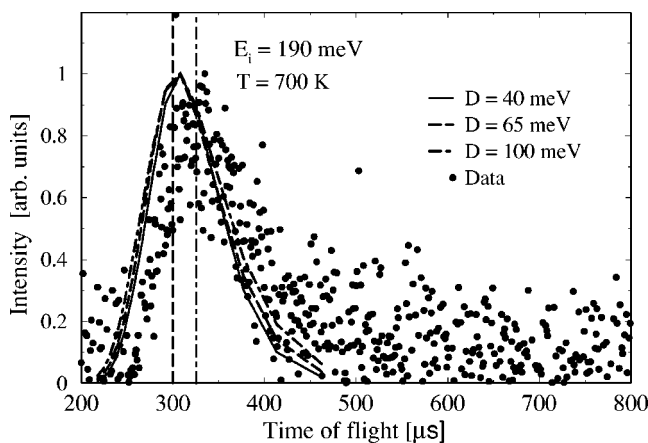


FIG. 6. Time-of-flight distributions for different values of potential well $D = 100, 65,$ and 40 meV as marked. The incident angle is $\theta_i = 45^\circ$, the translational energy is 190 meV, and the surface temperature is 700 K.

situation is somewhat less clear, in part because there is much more scatter in the data. The effect of a potential well is to broaden the calculated curves and to give a shift of the peak position to higher energies. Although a well depth of 40 meV gives a reasonable fit to the data, a somewhat larger well may be an even better choice. However, taking into consideration both sets of measurements, the angular distributions and the TOF spectra, the choice of $D=40$ meV which was used in Figs. 1 and 2 seems reasonable. This value is smaller than the binding energy for a full monolayer of CH_4 on Pt(111) as estimated from its measured desorption temperature of 67 K (Refs. 18,19) to be about 175 meV. Further measurements of the sticking coefficient indicate that the binding energy of an isolated CH_4 on a Pt(111) terrace could be in the range of 110–130 meV.¹⁸

In conclusion, it is shown that the theoretical model used earlier to describe the scattering of CH_4 from LiF(001) also provides a good explanation of the available data for scattering of CH_4 by Pt(111). The comparison of the theoretical model with the data produces an estimate of the physisorption well depth of the interaction potential that is somewhat smaller than that inferred from earlier thermal desorption and sticking experiments.

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- ¹S. Yagu, Y. Kino, K. Ozeki, and S. Yamamoto, *Surf. Sci.* **433–435**, 779 (1999).
²S. Yagu, T. Hiraoko, Y. Kino, and S. Yamamoto, *Appl. Surf. Sci.* **165**, 217 (2000).
³S. Yagu, Y. Kino, T. Hiraoko, M. Sasaki, and S. Yamamoto, *Appl. Surf. Sci.* **169–170**, 122 (2001).
⁴T. Kondo, T. Sasaki, and S. Yamamoto, *J. Chem. Phys.* **116**, 7673 (2002).
⁵T. Kondo, T. Sasaki, and S. Yamamoto, *J. Chem. Phys.* **118**, 760 (2003).
⁶T. Kondo (private communication).
⁷I. Moroz and J. R. Manson, *Phys. Rev. B* **69**, 205406 (2004).
⁸I. Iftimia and J. R. Manson, *Phys. Rev. Lett.* **87**, 093201 (2001).
⁹I. Iftimia and J. R. Manson, *Phys. Rev. B* **65**, 125401 (2002).
¹⁰I. Iftimia and J. R. Manson, *Phys. Rev. B* **65**, 125412 (2002).
¹¹H. Ambaye, J. R. Manson, O. Weiße, C. Wesenberg, M. Binteel and E. Hasselbrink, *J. Chem. Phys.* (to be published).
¹²R. Brako and D. M. Newns, *Phys. Rev. Lett.* **48**, 1859 (1982); R. Brako, *Surf. Sci.* **123**, 439, (1982).
¹³H.-D. Meyer and R. D. Levine, *Chem. Phys.* **85**, 189 (1984).
¹⁴E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill, New York, 1955).
¹⁵K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1970).
¹⁶L. A. Woodward, *Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy* (Oxford University Press, Oxford, 1972).
¹⁷A. Muis and J. R. Manson, *J. Chem. Phys.* **111**, 730 (1999).
¹⁸A. F. Carlsson and R. J. Madix, *Surf. Sci.* **458**, 91 (2000).
¹⁹V. A. Ukraintsev and I. Harrison, *J. Chem. Phys.* **98**, 5971 (1994).