Energy Dissipation of CH_4 Molecules by Inelastic Collisions at a LiF(100) Surface

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Abstract

Inelastic scattering of CH_4 molecules from a LiF(100) single crystal surface has been studied by using a supersonic molecular beam with variable kinetic energies. The result indicates that the LiF(100) surface behaves as if the mass is much larger than the actual and that the corrugation in potential energy surface seen by CH_4 molecules is different for different azimuthal incidence. For [100] incidence, a classical rainbow due to corrugation can even be observed. It is pointed out that in understanding fundamental chemical reactions such as dissociative adsorption of CH_4, intensive study is necessary towards understanding of the role of inelastic collision events.

1. Introduction

Surface properties, such as catalytic reactivity, adhesion, friction, corrosion, surface electrical and thermal conductivities, electron emission property and so on, are strongly relying on the surface electronic structures, which are uniquely determined by surface atomic structures. Hence, improving such properties as catalytic reactivity, requires choosing and/or modifying the surface atomic structures. In the field of thermionic electron emission, a great deal of efforts have been paid to reduce the work function by choosing and modifying the surface atomic structures. In these cases, it is necessary that modification of surface structure is performed in monoatomic order in accuracy and that the surface structure thus obtained be monitored and evaluated with monoatomic order in sensitivity without disturbing the structure.

Molecular beam scattering technique has recently attracted a great deal of attention because this technique gives us information concerning the dynamics of surface chemical reactions. This technique can also be applied to modify the surface structure. Here, we propose a new technique, where atoms are deposited and the structure monitored by a supersonic molecular beam without perturbation. In this technique, deposition is made by decomposition by collision of molecules, and monitoring the structure is made by He beam diffractive scattering. Decomposition by collision is a type of decomposition of molecules induced by collision with solid surfaces. Here the translational energy of the molecule is used to overcome the potential barrier for decomposition. Atoms thus decomposed deposit on the surface to modify the surface monoatomic structure. With this technique, large area modification in short time will be possible.

2. Modification of Surface Atomic Structures

A question arises whether desired site selective deposition is possible by a supersonic molecular beam. This is an essential requirement to modify surface atomic structures. Substrate atomic species on which atoms are deposited can be selected by the normal kinetic energy of impinging atoms. For example methane molecules are dissociatively adsorbed on a certain metal surface depending on their normal kinetic energy.1) Activation energy for dissociation probability depends on crystal orientation. For example, hydrogen molecules dissociate with different activation energy on copper single crystal surfaces of various orientations.2) There are different activation barrier heights for different adsorption sites on a single crystal plane. Adsorption sites may be able to be selected by carefully controlling the normal kinetic energy of impinging molecules. In all cases dissociative adsorption should be an activated process, otherwise such selection as substrate atomic species, crystal orientations, and adsorption sites will not be possible with decomposition by collision.

3. Energy Transfer Required for Decomposition by Collision

Upon colliding the surface a part of the kinetic energy of molecules is transferred into the surface by exciting phonons and at the same time, by exciting internal modes of molecules. The rest of the kinetic energy is spent to overcome the activation barrier for decomposition. Madix group reported the dynamics of alkane activation on Ni(100) and pointed out that apparent increase in activation barrier for higher alkanes is explained by energy dissipation to the surface.3) They also pointed out that excitation of vibrational modes of molecules is insufficient to be responsible for the dissipation. Hall et al. also pointed out the importance of inelastic collision during dissociative chemisorption of O_2 on Cu(100).4) Therefore, the knowledge of inelastic collision is essential in dealing with selective deposition. Luntz et al. have treated C-H bond activation on metals theoretically based on a quantum dynamics model,5) where both inelastic collision and conversion to internal modes are included.

In order to make a molecular beam to achieve selective deposition there are several requirements to be met. First of all, beam kinetic energy should be variable in a wide range with high resolution. Kinetic energy of molecules can be varied by cooling and heating the nozzle as well as by diluting in He. Normal component of the kinetic energy can be controlled by adjusting the incident angle of the molecular beam. Secondly, beam energy spread should be as small as possible to select adsorption sites precisely. Thirdly, beam intensity should be high enough to make this technique realizable.

4. Experimental Apparatus

Experimental apparatus has been constructed keeping all these issues above in mind. Schematic of the experimental setup is shown in Fig. 1. Molecular beam is produced in the source chamber as an adiabatic expansion of the highly pressurized gas from a nozzle. The beam flux is set to 0.77 Torrl/s ~ 2.7×10^{19} atom/s for a 5μm nozzle diameter at the source pressure of 100 atms . After passing through a 0.2mm skimmer, the molecular beam passes into the chopper chamber where it can be chopped into 10μs pulses for time-of-flight measurements. Upon passing through a1.17mm aperture, the molecular beam collides with the target in the scattering chamber usually kept under ultra high vacuum. On the target, the beam subtends an angle of 0.8° and makes a spot of 2.8mm on the sample. The sample temperature can be varied from 150 to 1200K. A differentially pumped six-axis manipulator allows rotations of θ and ϕ without disturbing the alignment of the target with respect to the center of the scattering chamber. The sum of the incident and reflected angles is 90°. The scattered molecular beam is detected by a quadrupole mass spectrometer in the detector chamber. In the case of a time-of-flight distribution, the signal is counted in 1μs bins with a multi-channel scaler. Rotation of the sample and data acquisition are controlled by microcomputer.

Speed ratio is the ratio of the drift speed to the most probable speed after expansion and is inversely proportional to the energy dispersion ΔE/E. It is a function of a product of nozzle diameter d and source pressure p_0, and the source temperature T_0. In our experiment, the pressure was varied up to 100 atms and the source temperature from 173 to 400K. Speed ratio of Helium atomic beam obtained at 300K source temperature was 40, which corresponds to the energy resolution about 8 %. By reducing the nozzle temperature to 180K, the energy

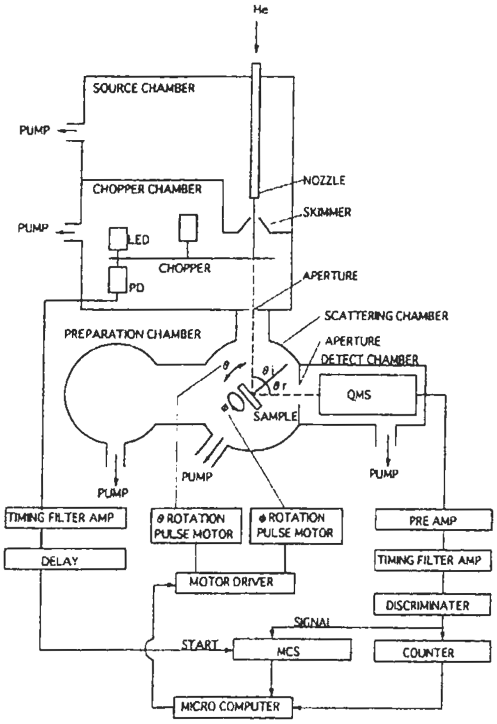

Fig. 1 Schematic of molecular beam scattering apparatus.

dispersion of 3% was possible.

5. Results and Discussions

A LiF(100) single crystal is chosen for the sample surface, because it is easy to cleave, no reconstruction is reported, and diffractive scattering of He from LiF is well known. Diffractive scattering of He beam from a LiF (100) single crystal surface for [110] and [100] azimuthal incident directions are measured, where the sample temperature is kept at 300K for the constant nozzle stagnation temperature of 180K. Lattice atomic distances obtained from the diffraction data agree with the reported. This technique allows us determining crystal azimuthal directions without disturbing surface structure, while other methods such as LEED and RHEED easily destroy the surface structures of monoatomic order during measurements.

Methane molecular beam scattering has been tried to study dissociative adsorption at a LiF surface. Angular distribution is measured of methane molecular beam scattered from a LiF(100) single crystal clean surface for [110] azimuthal incident direction for various incident beam energies and surface temperatures. Incident energy is controlled in a wide range by varying the nozzle temperature and the He mixture ratio. Fig. 2 shows the angular distributions of methane scattered from the LiF(100) surface kept at 300K for various incident energies. In contrast to He atomic beam diffraction, scattered methane molecular beam produce a broad angular distribution. The peak position of the distribution shifts towards higher angles for higher incident energies. Fig. 3 shows the change in the angular distribution for various sample temperatures for a fixed incident energy at 190 meV. No appreciable shift in the peak position can be observed in this case.

These results are compared with a classical theoretical model, the Hard Cube model proposed by Logan and Stickney.[6)] The reason for choosing this model is that the expression for spatial distribution of scattered beam is given in a simple analytical form. The spatial distribution of scattered methane molecules predicted by the model for monoenergetic incident beam is shown in Fig. 4. Our data

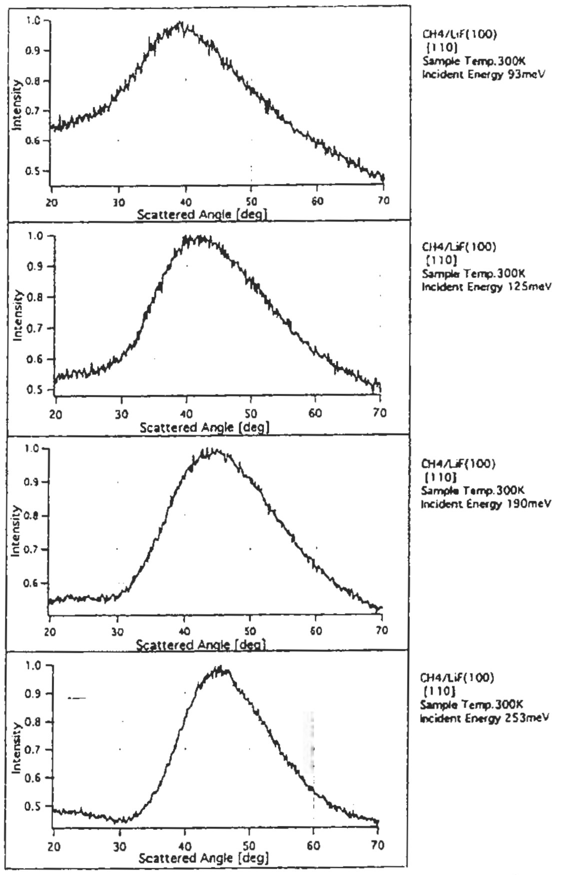

Fig. 2 Angular distribution of CH_4 molecules from a LiF(100) single crystal surface at room temperature for [110] azimuthal incident direction for various incident beam energies.

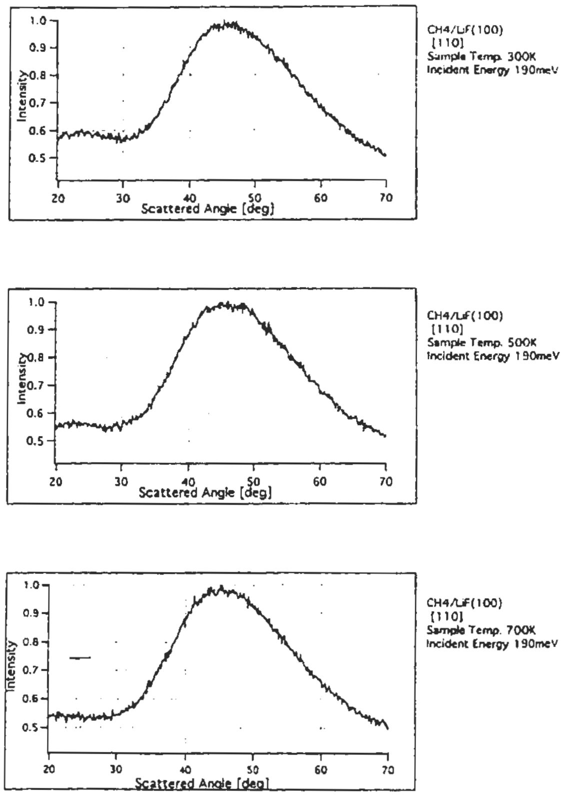

Fig. 3 Angular distribution of CH_4 molecules from a LiF(100) single crystal surface at various temperatures for [110] azimuthal incident direction for a constant beam energy 190 meV.

agree well with the model, as far as the peak position and the shift of the peak position are concerned, when the effective mass of the LiF single crystal surface is assumed to be that of platinum (M~195!). In fact, the spatial distribution of scattered methane molecules from a Pt(111) is very similar to ours.[7] This implies that LiF surface seen by methane molecules is heavy, hard and flat. The drift speed of methane molecules scattered from a LiF(100) single crystal surface is measured for various surface temperatures. The drift speed is obtained by fitting the time-of-flight data to the Maxwellian speed distribution function with a shifted drift speed. As shown in Fig. 5, qualitative agreement with the Hard Cube model prediction is good except at low scattered angles. The drift speed data indicates that methane seems to satisfy, to a certain extent, tangential momentum conservation law, which is the central assumption required for the Hard Cube model.

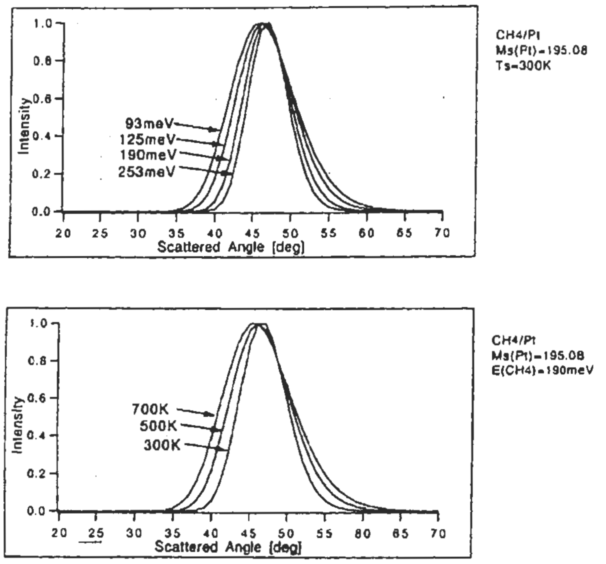

Fig. 4 Angular distribution of CH_4 molecules from a surface with the mass 195 predicted by the Hard Cube model for monoenergetic incident beam.

It is very interesting to see that as the azimuthal incident direction is varied by 45°, from [110] to [100], the drift speed data depart from the law of tangential momentum conservation as shown in Fig. 6. In this case, Hard Sphere model may be more appropriate to be examined, implying that the surface is hard and rough. Hard Sphere model predicts that the ratio of scattered beam speed to incident beam speed is given as a function of the mass ratio (incident beam mass and surface atom mass) and the sum of incident and reflected angles. Since the latter is constant in our experimental geometry, Hard Sphere model predicts a constant speed for the beam scattered at all angles. Corresponding spatial distributions for [100] azimuthal incidence are shown in Fig. 7, which are seen quite different from the previous distributions, showing two peaks in a distribution especially at low surface temperatures. These peaks can be understood as a result of classical Rainbow scattering. Assuming one dimensional potential energy surface with a sinusoidal hard wall corrugation of a period 0.402nm, being equal to the nearest neighbor F-F spacing, the corrugation amplitude of 0.016nm is obtained by fitting the data. The corrugated structure, however, disappears due to thermal smoothing as the temperature of the sample is raised. The role of surface corrugation is discussed theoretically in direct translationally activated dissociative

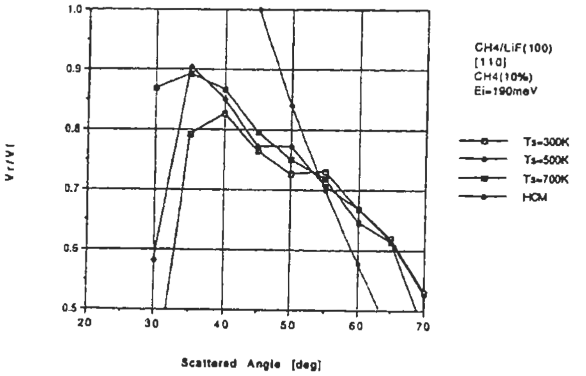

Fig. 5 Drift speed of scattered CH_4 molecules from a LiF(100) single crystal surface at various temperatures for [110] azimuthal incident direction for a constant beam energy 190 meV. The data are compared with the Hard Cube model prediction.

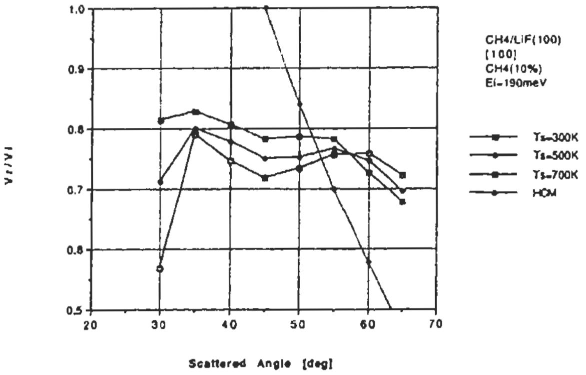

Fig. 6 Drift speed of scattered CH_4 molecules from a LiF(100) single crystal surface at various temperatures for [100] azimuthal incident direction for a constant beam energy 190 meV. The data are compared with the Hard Cube model prediction.

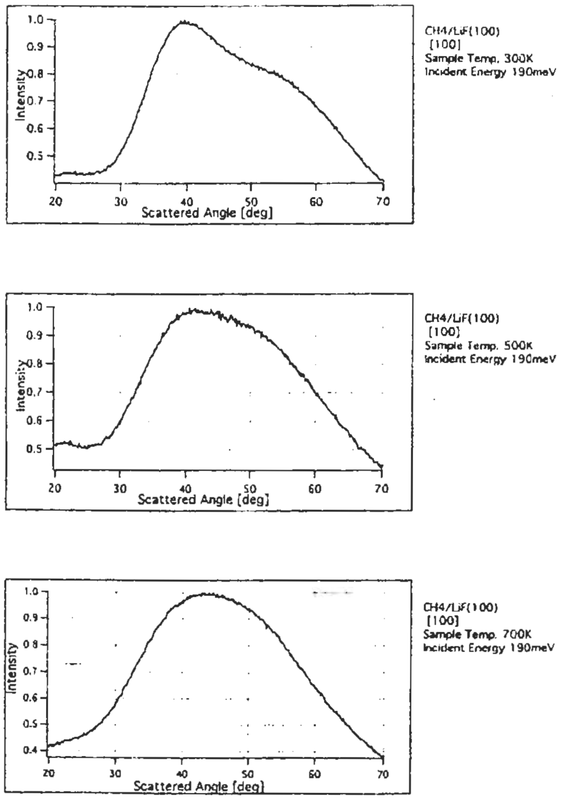

Fig. 7 Angular distribution of CH_4 molecules from a LiF(100) single crystal surface at various temperatures for [100] azimuthal incident direction for a constant beam energy 190meV.

adsorption.[8] It is pointed out that the kinetic energy directed along the local normal, in stead of the surface normal, controls the reaction probability.

From both measured spatial and speed distributions of scattered methane molecules, the energy dissipation can be estimated. Precise computation requires not only the in-plane but also out-of-plane scattering data. Our simple calculation based on the Hard Cube model, for smooth surface and for in-plane scattering, indicates that in the case of a Pt sample kept at room temperature, methane molecules with kinetic energies 83 and 300meV incident at 45° dissipate 6 and 10% of incident energy into the surface, respectively.

6. Conclusions

Inelastic scattering of the methane molecules from a LiF(100) single crystal surface has been studied by using a supersonic molecular beam with variable energies. For [110] incidence, the angular distribution agrees well with the Hard Cube model as far as the peak position and the shift of the peak position are concerned, when the effective mass of the LiF single crystal surface is assumed to be that of platinum (M~195!). The drift speed data indicates that the methane beam seems to satisfy, to a certain extent, the tangential momentum conservation law. For a smooth surface and for in-plane scattering, our calculation based on the Hard Cube model indicates that in the case of the sample with the mass number 195 kept at room temperature, methane molecules with kinetic energies 83 and 300meV, incident at 45° dissipate 6 and 10% of incident energy into the surface, respectively. The corresponding angular distributions for [100] incidence are seen quite different from the previous distributions, showing two peaks in the distribution especially at low surface temperatures. These peaks can be understood as a result of classical Rainbow scattering. The drift speed data departs from the law of tangential momentum conservation in this case.

It is pointed out that in understanding fundamental chemical reactions such as dissociative adsorption of methane molecules, intensive study is necessary towards the understanding the role of inelastic collision events.

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