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Abstract

A supersonic beam of H (or D) atoms, incident on a hot LiF(001) surface (T_{surf}=650-700 K), was used to study the reaction dynamics of H(D) + LiF(001). Time-of-flight spectra of HF and DF products show non-Boltzmann behavior; the translational energy distribution for each species peaks at higher energies than a Maxwell-Boltzmann distribution, indicating a barrier in the exit channel. For HF and DF, $\langle E \rangle_T$=4.3 kcal/mole, and the product translational energy distribution obtained suggests that both products leave the surface rotationally excited. By varying the angle between the LiF(001) surface plane and the beam, measurements of the θ_i distribution of products indicate that the newly formed diatomic has some "memory" of the incident beam. H(D) +

LiF(001) to form HF (or DF) is one of the few cases where the Eley-Rideal reaction mechanism has been observed. This work demonstrates the use of the molecular beam-surface scattering technique to directly measure the time-of-flight of individual reaction products as they form and evolve from the surface.

Introduction

Reactions at the gas-surface interface have been successfully probed using molecular beam techniques by many research groups. Modulated beams have been used to study the kinetics of gas-surface reactions by measuring the rates of formation of various product species as they evolve from the surface.[1-3] The dynamics of the gas-surface reaction can also be studied using molecular beam techniques. Pure adsorption and desorption events, which model important steps in the overall reaction process, have been more extensively studied than reaction product dynamics.[4] The final step in a gas-surface reaction, where either a bond is formed and/or the new product molecule desorbs from the surface, can be studied by looking at the product translational and/or internal energy as it emerges from the surface.[5] For example, the work on D_2O formation in the oxidation of deuterium on Pt(111) by Ceyer et. al.[6] shows how the D_2O product angular and translational energy distributions lead to an understanding of the reaction mechanism. The internal states of product CO_2 from CO oxidation on Pt have also been measured, showing how different modes, each characterized by its own Boltzmann temperature, behave as a function of surface temperature.[7]

In this work, the velocity distributions of individually mass-selected products are measured as they desorb from the surface for different angles between the source, a supersonic atomic beam of H or D

atoms, and the plane of the surface, LiF(001), with the detector fixed. In addition to identification of reaction products, analysis of this type of data reveals the dynamical nature of the gas-surface reaction.

Crystalline LiF is usually considered to be a relatively inert material. However, the gas phase reaction H + LiF ---> HF + Li is nearly thermoneutral.[8] In the solid phase, the LiF lattice commonly contains anion vacancies that can sometimes be filled by H-atoms without too much distortion of the total lattice electron density.[9] In addition, calculations show that as an H-atom approaches certain types of anion vacancies, a bound state is formed, whereas for H_2 the interaction is repulsive.[10] The interesting dynamics of the H-atom LiF(001) surface interaction explored here show that LiF(001) is not inert to H-atoms, and indeed the reaction product HF (and the DF analogue) is directly measured by time-of-flight methods.

Experimental

A continuous supersonic beam of H (or D) atoms was directed towards a freshly cleaved LiF(001) surface in a gas-surface scattering apparatus (Fig. 1), to be described in detail separately.[11] The particles scattered from the surface are chopped by a cross-correlation wheel, mass selected, and counted by a channeltron after travelling through a flight distance of 23.9cm.[12] Time-of-flight spectra of individual mass-selected

species are thus measured, which allows for determination of the translational energy imparted to individual products of a gas-surface chemical reaction. In this experiment, the isotopes of Ne at m/e= 20 and 22 were used to calibrate the mass spectrometer. Also, by using high resolution, m/e= 19, 20, and 21 could be clearly distinguished.

The H and D atoms are produced in a supersonic expansion by thermal pyrolysis of neat H_2 or D_2, using a high temperature nozzle made of pure rhenium metal (Sandvik Rhenium). The nozzle is made of two concentric rhenium tubes that are connected by a rhenium cap, which has been welded to one end under inert atmosphere. A 0.007" nozzle hole was drilled in the center of the cap by EDM (EDM Exotics). The inner tube is welded to 1/4" stainless steel tubing, which forms the gas line. Two water-cooled copper clamps, one attached to the inner rhenium tube and one to the outer tube, carry the current and secure the nozzle to a translational stage. The translational stage allows for thermal expansion of the rhenium tubes as they are heated without straining the welds at the cap. The current is thus forced to pass through the welded cap, where it can heat the metal to about 2500 K (using up to 250 W). The nozzle temperature has been measured using optical pyrometry and by measuring the beam time-of-flight for a neat Ne beam. The temperatures from the two measurements agree well (Fig. 2). The nozzle was operated at 2140 K to produce H and D atoms but minimize the

possibility of evaporating rhenium metal, which becomes a problem above 2500 K. The use of rhenium instead of tungsten, which has been used previously,[13] was motivated by a desire to find a material that does not become brittle and therefore susceptible to cracking after thermal cycling to high temperatures. The flux of H-atoms is determined to be 5×10^{18} atoms cm^{-2} s^{-1} based on a 3% dissociation rate of H_2 under the beam conditions used.

The LiF samples were cleaved from a single-crystal boule in air along the natural (001) cleavage plane. Freshly cleaved samples were heated in vacuum (1×10^{-7} Torr) for 24 hrs. at about 750 K to remove water and anneal the crystal. Experiments were typically run between 650-700 K to minimize adsorption of impurities. A narrow velocity distribution in the scattering pattern from H_2 is a good check of the cleanliness of the surface, and so such time-of-flight measurements were performed before looking for reaction products. The beam was brought to high temperature over the course of 2 hrs. and allowed to stabilize, with the crystal out of the beam path. Once the beam was stable, a typical time-of-flight spectrum of product HF or DF took about an hour or two to collect, depending on the angle between the beam and the surface plane. The angle θ_i, between the beam and the surface, and ϕ_i, the angle of the beam with respect to the [100] surface direction, can both be varied independently. No ϕ_i dependence was observed, though, in the case of

HF or DF product evolution, so the spectra in the figures here are all at $\phi_i = 0°$. The angle θ_i is defined to be 0° when the angle between the beam and the surface plane is 0° (it is the complement of the angle between the beam and the surface normal); the detector is fixed at 90° from the beam.

Results

HF(m/e= 20) and DF(m/e= 21) product time-of-flight spectra were measured in separate experiments for different angles, θ_i, between the source and the plane of the LiF(001) surface. The product DF has the advantage that m/e= 21 has very low background in the mass spectrometer. In addition to monitoring the appropriate product mass, spectra were also taken at m/e= 19, corresponding to fluorine, and also m/e= 1 or 2 resulting from reflected H and H_2 or D and D_2, respectively. The product m/e= 20 or 21 signal was only seen when the nozzle was hot enough to produce atomic H or D, and considerable effort was made to keep the experimental conditions the same between HF and DF experiments so that they could be compared. At a nozzle temperature of 2140 K, the maximum H or D atom beam energy is calculated to be ~7.5 kcal/mole.[14]

Typical time-of-flight spectra at m/e= 20 for H + LiF(001) and at m/e= 21 for D + LiF(001) are shown for $\theta_i = 30°$ along with the time-of-

flight for the reflected beam in each case in Fig. 3. The m/e= 20 and 21 time-of-flight spectra show a sharp fast peak and a slower peak. The time-of-flight for the reflected beam in each case has been scaled and shifted to have the same leading edge as the m/e= 20 or 21 data to clearly show that the peak from the beam is narrower. The origin of the fast peak will be addressed in the discussion of the results, but at this point suffice it to say that the slow peak is the only real product signal.

At all angles θ_i, the HF or DF product time-of-flight is the same as that of m/e= 19, corresponding to F. The matching time-of-flights indicate that F results from cracking of HF or DF in the ionizer rather than by other mechanisms, such as desorption of F or LiF from the surface. Such a desorption mechanism should give rise to a Maxwell-Boltzmann distribution at the surface temperature, which would extend out to longer times in the time-of-flight spectrum. No evidence for this type of mechanism was observed.

Fig. 4 and Fig. 5 show the time-of-flight spectra obtained at m/e= 20 and m/e= 21, respectively, for different values of θ_i. Also included in the figures are simulated time-of-flight spectra for the slow peak, corresponding to the translational energy distribution in Fig. 6. Each frame has been scaled to show the details of the individual spectra; the change in product yield with θ_i is shown separately in Fig. 7. The simulated spectra are obtained by the forward convolution method[15] and

include the various apparatus functions that affect a time-of-flight spectrum. In this case, since the fast peak in the product time-of-flight spectra could not simply be removed by subtracting the corresponding reflected beam time-of-flight (due to the different peak widths, see discussion), simulations of the slow peak were done by generating a consistent translational energy distribution at all angles θ_i. For both products, HF and DF, one translational energy distribution that fits the slow time-of-flight peak was found (Fig. 6) with $\langle E \rangle_T = 4.3$ kcal/mole and $E_{max} = 13$ kcal/mole. In the region of the peak maximum, the uncertainty is 0.2 kcal/mole, but at E_{max} (tail of the distribution) the uncertainty is as high as 1.3 kcal/mole. The cross-correlation wheel is limited to 5 μsec time resolution, and the energy goes as $E \propto (1/t)^2$, giving rise to greater uncertainties at higher energies.

A θ_i distribution is calculated by integrating under the curve for the simulated time-of-flight peak in each spectrum. The HF and DF θ_i distributions look similar (Fig. 7), peaking near $\theta_i = 45\text{-}50°$. Although these distributions are not full flux angular distributions, given the geometry of the machine, they do indicate that the scattering lobe for the product HF or DF lies near the specular angle.

Discussion

Atomic Reactant Species

The fact that HF or DF product is not seen until the beam source nozzle is hot enough to dissociate a significant fraction of H_2 or D_2 strongly suggests that the atomic species is indeed the reactant in the systems discussed here. Calculations done by Matsumura support this conclusion.[16] The calculations show that for H_2 approaching anion vacancies in the LiF lattice at either an edge, corner, or surface vacancy, the interaction is highly repulsive. For atomic H, however, there is an attractive interaction, especially when an electron is trapped in the vacancy. H_2 approaching a site on the LiF(001) surface with no vacancy would also not be expected to molecularly adsorb and take part in a reaction. In addition, dissociative chemisorption of H_2 is not possible because the dissociative adsorption energy of 1 eV is smaller than the 2.3 eV necessary to break the H-H bond. Therefore, the atomic species produced in the beam must be the reactant.

Origin of the Fast Time-of-Flight Peak

In the time-of-flight spectra of Fig. 4 and Fig. 5, there are clearly two peaks. The fast peak is largest at θ_i= 45° (not shown), where it completely hides the features of the second, slow peak. As θ_i is moved towards a grazing angle of 10° or near the surface normal at 80°, the fast peak drops to a minimum and the second, slow peak becomes the dominant feature. The fast peak, when converted to a translational

energy distribution, extends out to energies as high as 40 kcal/mole for the case of HF. HF coming off the surface with 40 kcal/mole of translational energy is not physically reasonable, and so other sources of the fast time-of-flight peak must be considered.

In the source, H or D atoms are produced, which can be excited in the electron bombardment ionizer to Rydberg states. In fact, even H_2 can be a source of excited states of atomic hydrogen in the electron bombardment ionizer.[17] Such Rydberg H or D atoms are energetic neutrals, travelling with the velocity of the beam. As neutrals, they cannot be filtered by the quadrupole, but they can be detected by the channeltron; thus, they show up in spectra taken at m/e= 20 or 21. In fact, if the fast time-of-flight peak is due solely to Rydberg atoms, it should appear at any mass setting on the quadrupole, and so by tuning to masses not normally expected to produce signal, this hypothesis can be tested. Upon tuning to other m/e settings of the quadrupole, however, the fast peak did not always appear. In fact, it only appeared at masses where there was significant background in the mass spectrometer or where the reaction product HF or DF appeared. Thus, Rydberg H or D atoms alone cannot fully explain the presence of the fast time-of-flight peak.

The fact that the fast time-of-flight peak is observed at masses where background appears offers a clue. H^+, metastable H_2,[18] and

Rydberg H-atoms (all produced by electron impact) can ionize background gases through collisions just after the ionization region in the detector (and before the quadrupole mass filter). There is a constant source of background because a continuous beam and a cross-correlation chopper wheel are used in the experiment. Two processes can occur to give rise to signal at background masses. First of all, H^+ formed in the ionizer can undergo charge exchange collisions that ionize background gas molecules.[19] Secondly, through processes such as Penning ionization and associative ionization, the background molecules can be ionized by Rydberg H (D) atoms or metastable H_2 (D_2) and therefore mass-selected by the quadrupole.[20] They appear in the time-of-flight spectrum at the characteristic time of the excited H, D, H_2, or D_2, which is very fast. In comparing the reflected beam time-of-flight with the fast peak due to collisional ionization (Fig. 2) the collisional ionization peak is broader, but it is reasonable that the collisional process would give rise to broadening since the background molecules are moving at random velocities and the collisions occur with a wide range of impact parameters. All of the above mechanisms may be operating simultaneously, but the density of H_2 (D_2) is much greater than H (D), and so charge exchange from the molecular species is probably contributing more to the fast time-of-flight peak than atomic species involved in Penning and associative ionization processes.

In comparing the collisional ionization effect from different spectra, it is interesting to note the intensity dependence of the fast time-of-flight peak on the mass-selected species and the angle θ_i, which determines how much of the incident beam is directly reflected into the detector. In comparing spectra for different mass-selected species, the highest intensity is seen for m/e= 28, which is usually the highest background mass peak in any vacuum system and normally attributed to CO. For θ_i= 45°, the ratio of the fast peak for the m/e= 28 spectra to that of the m/e= 21 (product DF) spectra is 5:1. The intensity of the fast peak seen in spectra taken at m/e= 18 is only 4% of the m/e= 28 peak, which is consistent with a low background due to residual H_2O in the vacuum. In the m/e= 21 spectra, there is a strong dependence of the collisional ionization peak intensity on the angle θ_i. The intensity of the collisional ionization peak drops by a factor of 4 when changing from θ_i= 30° to θ_i= 20°, but the intensity of the slow peak due to the products remains the same. The angular dependence shows that the fast time-of-flight peak has a strong dependence on the incident beam, as expected for the collisional ionization mechanism.

The arguments above rule out the possibility of the fast peak arising from reaction products formed at the surface, which is the main interest in this experiment. Attention is thus focused on the slower peak, which is why a fit for only the second peaks and the corresponding

translational energy distribution is displayed in Figs. 4-6.

Dynamics of HF and DF Products

The HF and DF reaction products, measured directly as they evolve from the surface, appear as the slower peaks in the time-of-flight spectra of Figs. 4 and 5, respectively. The translational energy distribution in Fig. 6 is derived by fitting the slow peak for both products at each angle θ_i. The difficulty in this method is finding the true leading edge of the slow peak, which corresponds to the high energy limit of the translational energy distribution. However, at $\theta_i = 10°$, the leading edge is distinguishable since the signal between the first and second peaks drops to the baseline. The same translational energy distribution is used to fit the data from both reactions at all angles θ_i.

The translational energy distribution for HF and DF is not a Maxwell-Boltzmann distribution at the surface temperature. Fig. 8 compares the product translational energy distribution from Fig. 6 with a Maxwell-Boltzmann distribution at the surface temperature, $T_{surf} = 690$ K. The product distribution peaks at higher energy than a Maxwell-Boltzmann distribution, about 2.5 kcal/mole, with a substantial fraction of the molecules having up to 13 kcal/mole of translational energy. The translational energy distribution peaking far from the Maxwell-Boltzmann distribution peak indicates that there is a barrier in the exit

channel.

Although it is possible to fit the HF and DF products separately so that they each have their own translational energy distribution, such a distinction between the products is not strongly supported by the data. The difference in the energy distributions is too small to be justified given the signal/noise ratio and the added complication of the collisional ionization peak near the leading edge of the product time-of-flight peak. However, it is interesting to note that when two distributions are used, best fit to all the θ_i for a particular product, the DF appears to have less energy left over in translation than the HF upon separating from the LiF(001) surface (although the two distributions have the same E_{max}). This suggests that DF has more energy in rotational degrees of freedom, which is not surprising considering the rotational constants B_{HF}= 20.939 cm^{-1} and B_{DF}= 11.007cm^{-1}.[21] Only one translational energy distribution is used to fit both the HF and DF data here, though, which is reasonable since the features of the potential energy surface influencing the dynamics should be the same.

If the total available energy for the reaction to make HF or DF were known, then the translational energy distribution would give more detailed information about the internal states of the product molecules. This in turn would reveal some details of the reaction mechanism. However, the energy required to form and remove the HF or DF molecule

is not known. If, for the sake of forming a qualitative picture, one assumes the maximum energy in the translational energy distribution is also the total available energy to the product HF or DF, and that the products are all in v= 0, then the rotational states lying under the distribution of Fig. 6 can be as high as J= 14 for HF and J= 20 for DF.[22] Since the vibrational spacing for HF is 11.83 kcal/mole, it is unlikely that any vibrational excitation occurs. For DF, the vibrational spacing is lower, 8.57 kcal/mole, so it might be energetically possible to have some vibrational excitation. The shape of the translational energy distribution does not support this conclusion, though. Qualitatively, the rotational excitation indicates that in the exit trajectory off the surface, the potential exerts some torque on the molecule. However, there are certainly other factors leading to the broadening of the time-of-flight spectrum, so the J values are not a strict assignment. For example, a variety of surface sites leading to reaction will broaden the product distribution.

The fact that HF and DF have the same maximum energy gives a clue about the microscopic picture of the molecule's departure from the surface. Two extreme cases can be considered. First, if the "kick" off the surface is directed to the light end of the diatomic product, the translational energy distributions for HF and DF, particularly the E_{max}, will be different depending on whether H or D receives the "kick" (Fig. 9).

In fact, DF should have about four times the kinetic energy of HF in this scenario (a factor of 2 from v_D^2 and a factor of 2 from M_D). In the second case, however, if the heavy fluorine end gets the "kick" then the translational energy distributions will be about the same for HF and DF, which is what is observed in the experiment. Thus in this picture, if a strong torque is exerted to one end of the product by the potential, it must be applied toward the fluorine rather than the H or D end of the diatomic product. However, in the case of HF and DF the center-of-mass is very close to the fluorine end of the molecule, so if the repulsion is applied toward the center-of-mass, a similar E_{max} would also be observed. It is safe to say, though, that a strong torque is not applied to the light end of the product HF or DF.

The θ_i distributions for HF and DF in Fig. 7 are peaked with their maxima near the specular angle. Fig. 10 shows the experimental θ_i distribution for HF and a cosine distribution. The cosine distribution would be observed if: 1) the desorbing product had no "memory" of the incident beam and 2) the desorbing product molecule was completely in equilibrium with the surface, at the surface temperature of 690 K. Clearly, the two distributions are different. The experimental distribution is highly peaked towards 45-50° (angle between the detector and the surface normal, which is equal to θ_i). A simple fit to a $\cos^n\theta$

function is not appropriate, however, since $E_\perp$ (the component of the beam energy normal to the surface) changes with θ_i (i.e. as the surface is rotated the incident and final angles are changed simultaneously). It can be concluded, however, that the angular distribution has some dependence on the incident atomic beam angle, and hence $E_\perp$. Thus, the product molecule does have some "memory" of the incident beam. This indicates that the HF and DF are formed through an Eley-Rideal mechanism, which is fairly unusual. Most gas-surface reactions are of the Langmuir-Hinshelwood type.[23-25]

Surface Reaction Mechanism

The possibility of surface roughening as a result of the reactions with H and D atoms was investigated. The H_2 or D_2 time-of-flight patterns from the reflected beam should be sensitive to surface roughness. A less well-ordered surface will give a broader time-of-flight pattern. However, comparison of HF or DF time-of-flight spectra before and after 3 hours of reaction at the same spot on the surface showed no evidence for surface roughening.

The nature of the surface site in this reaction is unknown. The LiF(001) surface has steps and terraces as well as anion vacancies. The vacancies may have an electron trapped in them. The different sites are expected to have different reactivities. Matsumura's calculations[26] clearly

show that for anion vacancies, depending on the type (with or without a trapped electron) and location (i.e. corner, edge, or surface), the H-atom will feel a different potential. For example, the energy for adsorption of an H-atom on a surface vacancy with a trapped electron is as high as -6.266 eV, and the H sits in the lattice as H^- where it mimics the missing F^-. On the other hand, an H-atom interacting with the same vacancy without a trapped electron has an adsorption energy of only -0.062 eV, and the potential curve is largely repulsive. Similar differences in the corner and edge sites are reported. Since the HF and DF in this experiment leave the surface with up to 13 kcal/mole of translational energy, it seems unlikely that the trapped electron vacancy is the site of reaction. If the H can sit in the lattice as H^-, then formation of HF that leaves with excess kinetic energy should be unfavorable. Also, the F that the H reacts with would have to be either an interstitial F or one diffusing along the surface, because in a "perfect" lattice the H would only see Li neighbors. More likely, the HF or DF is formed at sites where the H or D atom cannot easily replace F in the lattice, and then the newly formed molecule feels a repulsive potential as it leaves the surface. The question remains, though, whether H reacts at an anion vacancy site (without a trapped electron) or creates one by pulling F out of the lattice.

Conclusions

A supersonic beam of H or D atoms incident on a LiF(001) surface can be used to study the dynamics of the HF or DF product formed. By directly measuring the time-of-flight of the product species as it evolves from the surface, features of the potential energy surface involved are elucidated. The translational energy distribution describing both products peaks higher in energy than a Maxwell-Boltzmann distribution, indicating that there is a barrier in the exit channel for HF and DF to form and evolve from the surface. There is also evidence of rotational excitation, and a microscopic picture of the molecule-surface interaction is discussed . However, because the energetics of the reaction are unknown in this case, details about the internal states of the products cannot be resolved. A state-specific study of the reaction products could help to further understand the details of the surface reaction mechanism.

With an ultra-high vacuum system, the reaction could be explored over a wide range of surface temperatures. Here, surface temperatures were limited to 650-700 K to insure cleanliness of the crystal surface. In addition, when the H or D atom hits the surface it has ~7.5 kcal/mole of translational energy from the beam, chiefly determined by the nozzle temperature. A study of the role of energy transfer in the reaction by varying the H or D collision energy would be interesting, but accelerating H or D atoms is not a trivial problem. As new sources of H

and D atoms are developed, perhaps such an investigation will be possible.

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[26] see Ref. 9.

Figure Captions

Fig. 1 Gas-Surface Scattering Apparatus with channeltron (A), exit lenses (B), liquid nitrogen cooled copper insert (C), quadrupole filter (D), Brink type electron bombardment ionizer followed by entrance lenses (E), high-temperature rhenium nozzle (F), surface mounted on 3-axis rotatable manipulator (not shown) (G), cross-correlation chopper wheel (H), source region pumped by 6000 l/s diffusion pump (I), differential region pumped by 1000 l/s diffusion pump (J), main chamber pumped by two 2000 l/s diffusion pumps equipped with liquid nitrogen baffles (K, L), three regions of differential pumping on the detector pumped by three 400 l/s magnetically suspended turbomolecular pumps (T1, T2, T3).

Fig. 2 Nozzle temperature as a function of power. Temperature calculated from neat Ne beam time-of-flight (circles) and measured by optical pyrometry (squares).

Fig. 3 Time-of-flight spectra at $\theta_i = 30°$ comparing the width of the reflected beam with the width of the fast time-of-flight peak due to collisional effects (see text): (a) H-atom beam (solid line) compared to m/e=20 signal (circles), and (b) D-atom beam (solid line) compared to

m/e=21 signal (circles).

Fig. 4 m/e=20 time-of-flight spectra (circles) showing the second peak fit at all angles, θ_i, by a simulated time-of-flight spectrum (solid line) generated from one translational energy distribution, shown in Fig. 6. The collisional ionization component shown (.....) is not a fit.

Fig. 5 m/e=21 time-of-flight spectra (circles) showing the second peak fit at all angles, θ_i, by a simulated time-of-flight spectrum (solid line) generated from one translational energy distribution, shown in Fig. 6. The collisional ionization component shown (.....) is not a fit.

Fig. 6 Translational energy distribution used to fit HF and DF data in Figs. 4 and 5; $\langle E \rangle_T = 4.3$ kcal/mole.

Fig. 7 θ_i distributions for HF (filled circles) and DF (open circles) calculated by integrating the simulated time-of-flight spectra for each angle θ_i.

Fig. 8 HF translational energy distribution (solid line) compared to a Maxwell-Boltzmann distribution for the surface temperature, $T_{surf} = 690$ K (dashed line). The distributions are normalized.

Fig. 9 Microscopic picture of the fluorine end of the diatomic product feeling the "kick" off the surface, justified by HF and DF having the same E_{max}.

Fig. 10 Polar plot showing the measured θ_i distribution for HF (triangles) and a cosine distribution expected if HF were in equilibrium with the surface (squares). For the measured distribution, the normal component of the incident enegy ($E_\perp$) changes with θ_i. For Detection Angle 1 $E_\perp$= 2.6 kcal/mole, while for Detection Angle 2 $E_\perp$= 6.6 kcal/mole.

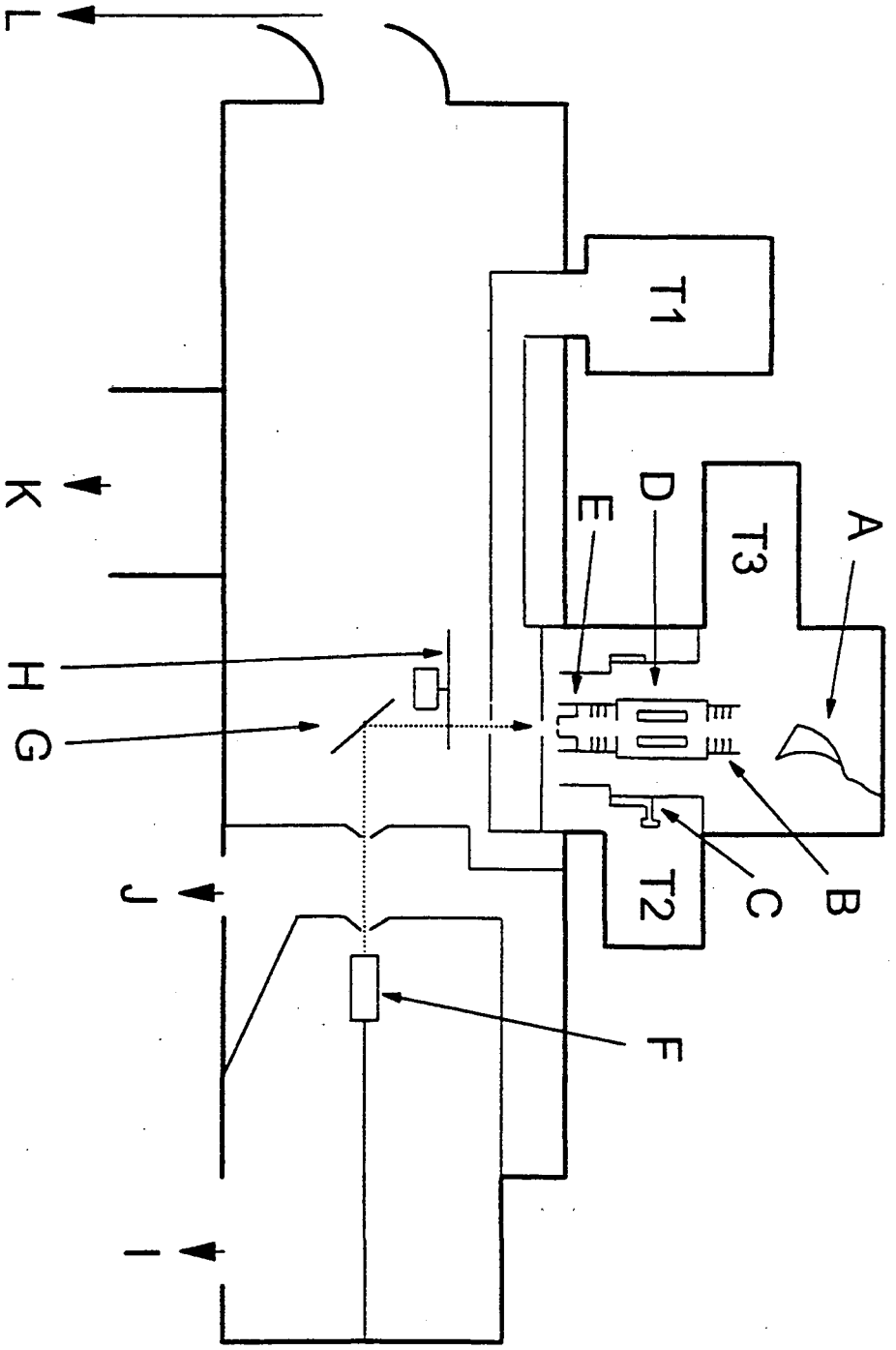


Fig. 1, L. A. Smoliar, J. Chem. Phys.

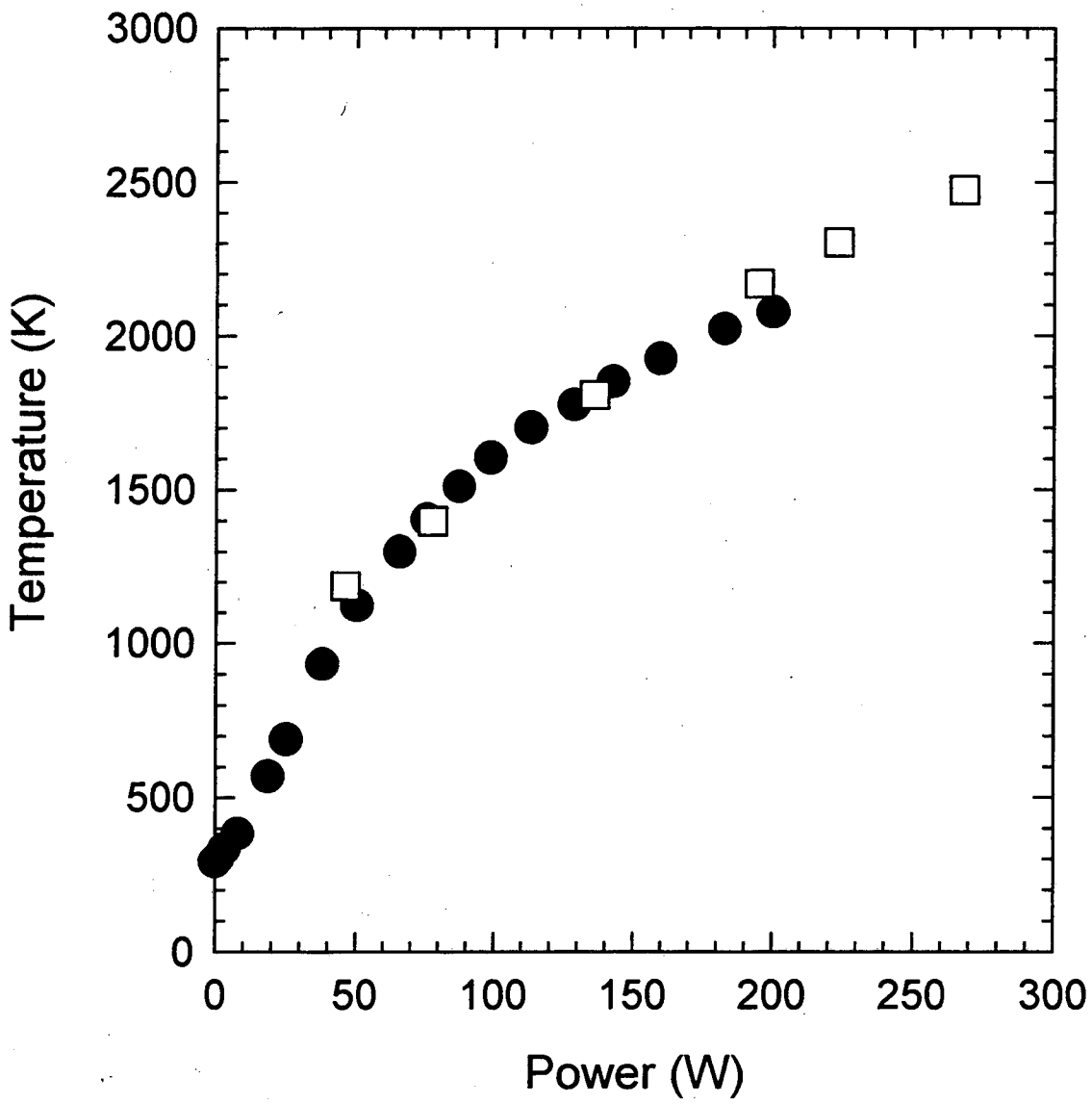


Fig. 2, L. A. Smoliar, J. Chem. Phys.

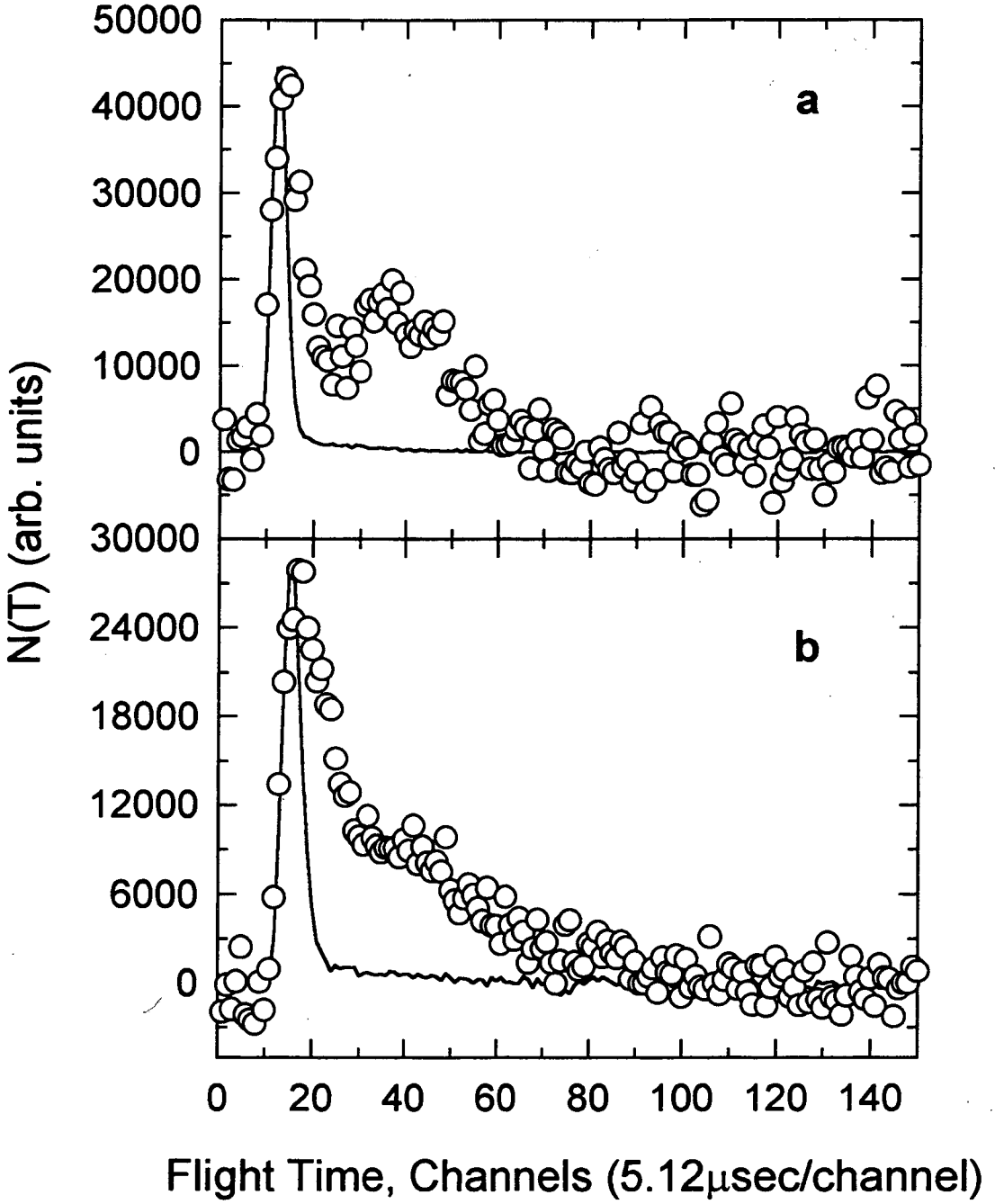


Fig. 3, L. A. Smoliar, J. Chem. Phys.

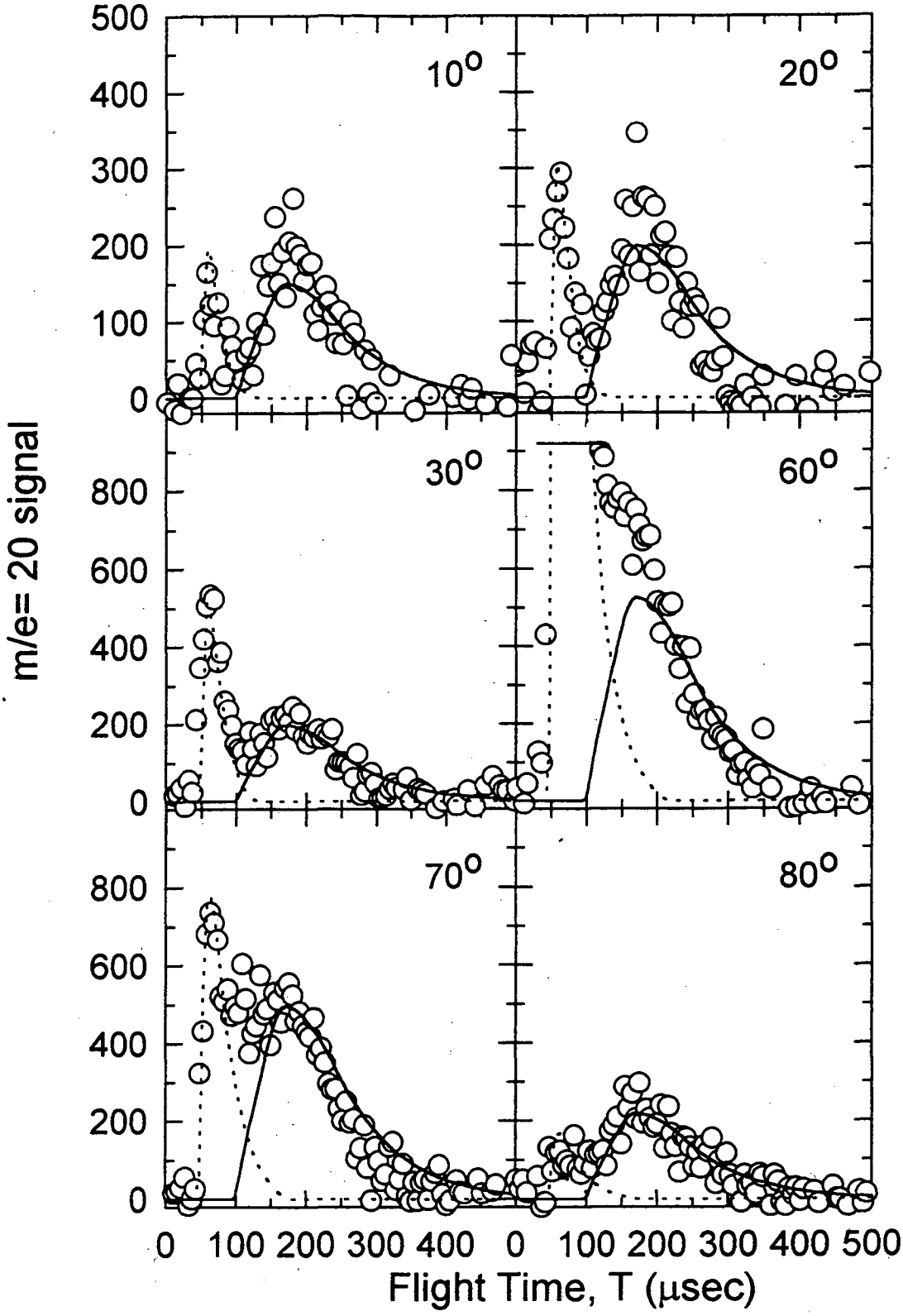


Fig. 4, L. A. Smoliar, J. Chem. Phys.

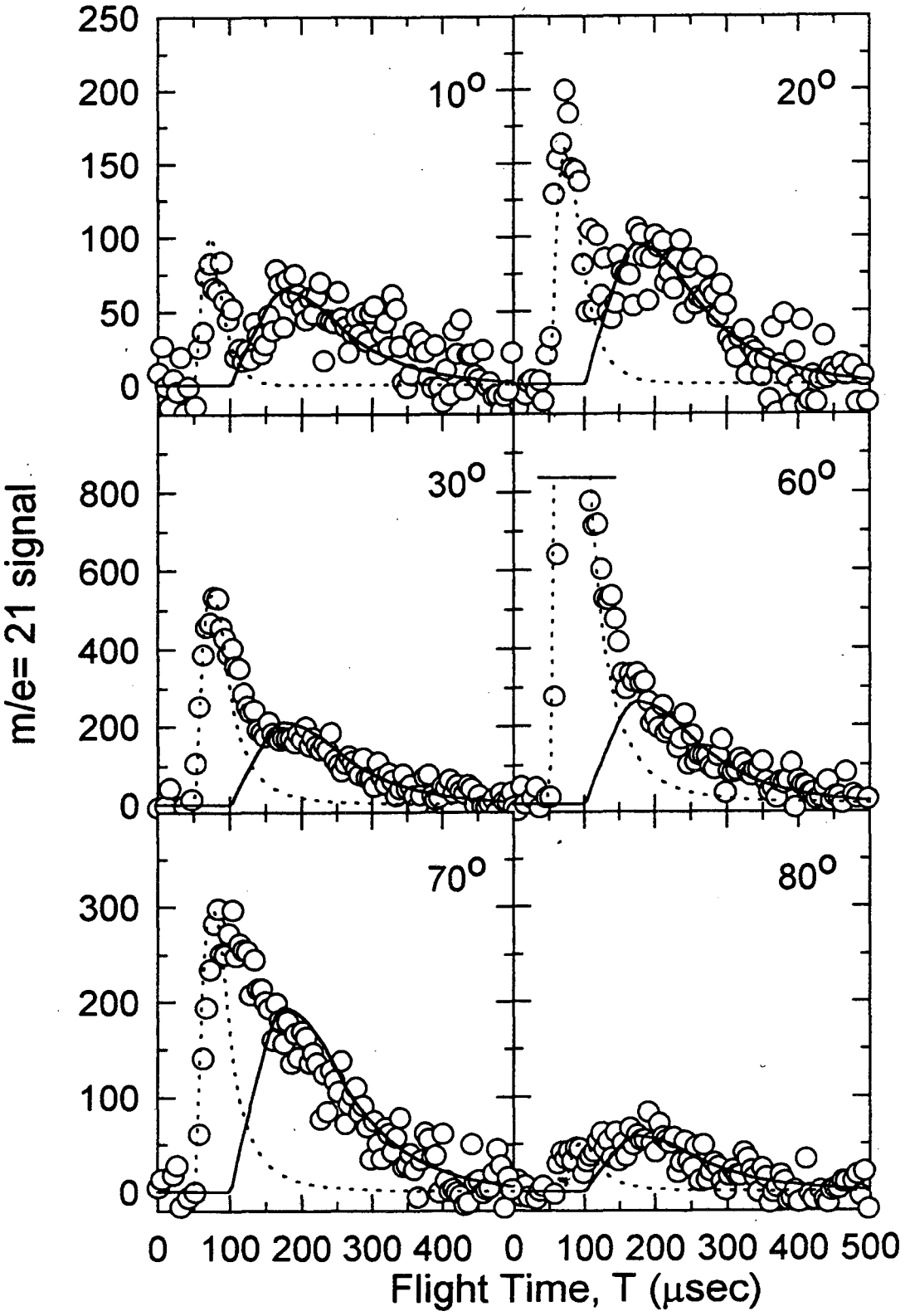


Fig. 5, L. A. Smoliar, J. Chem. Phys.

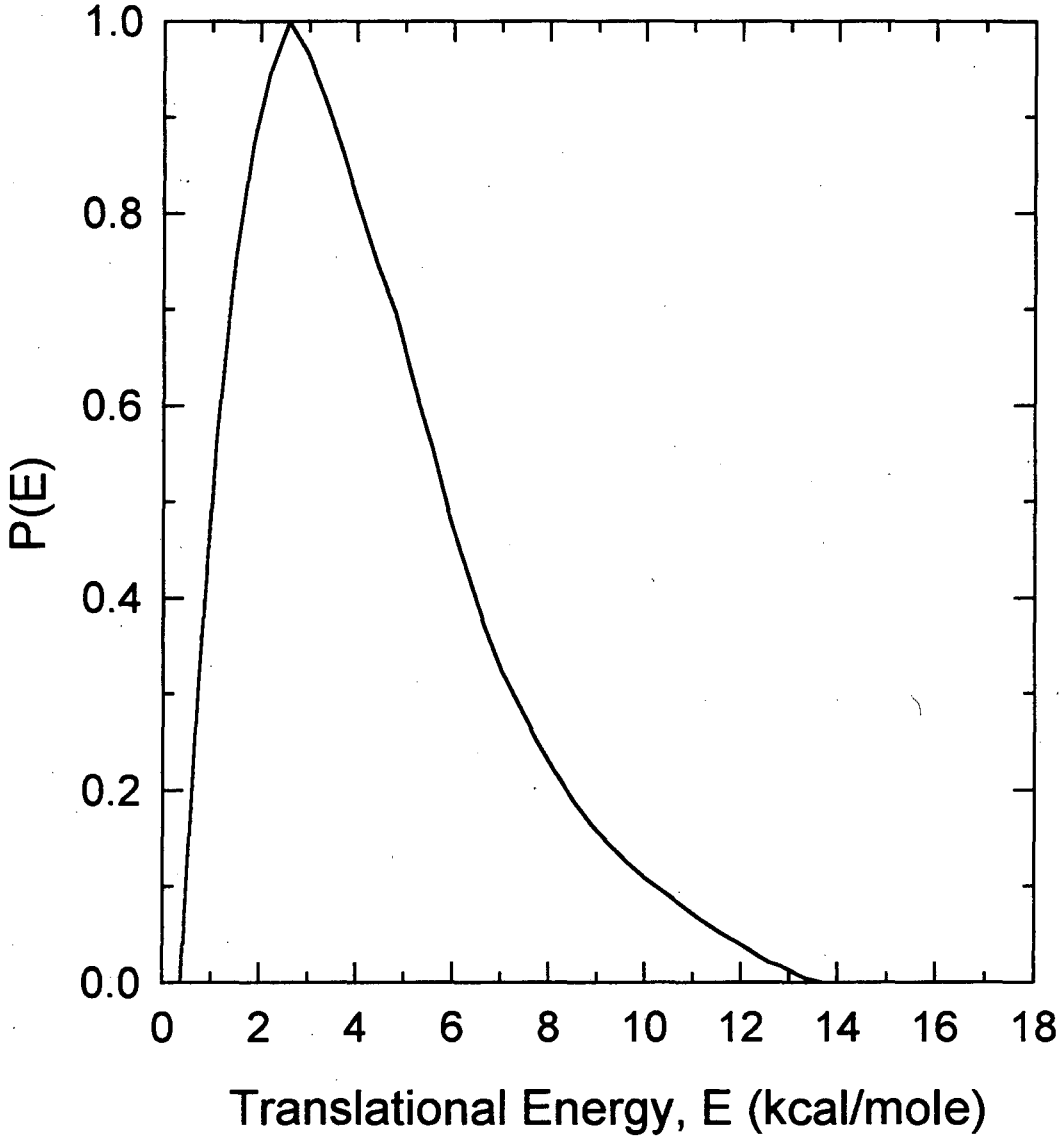


Fig. 6, L. A. Smoliar, J. Chem. Phys.

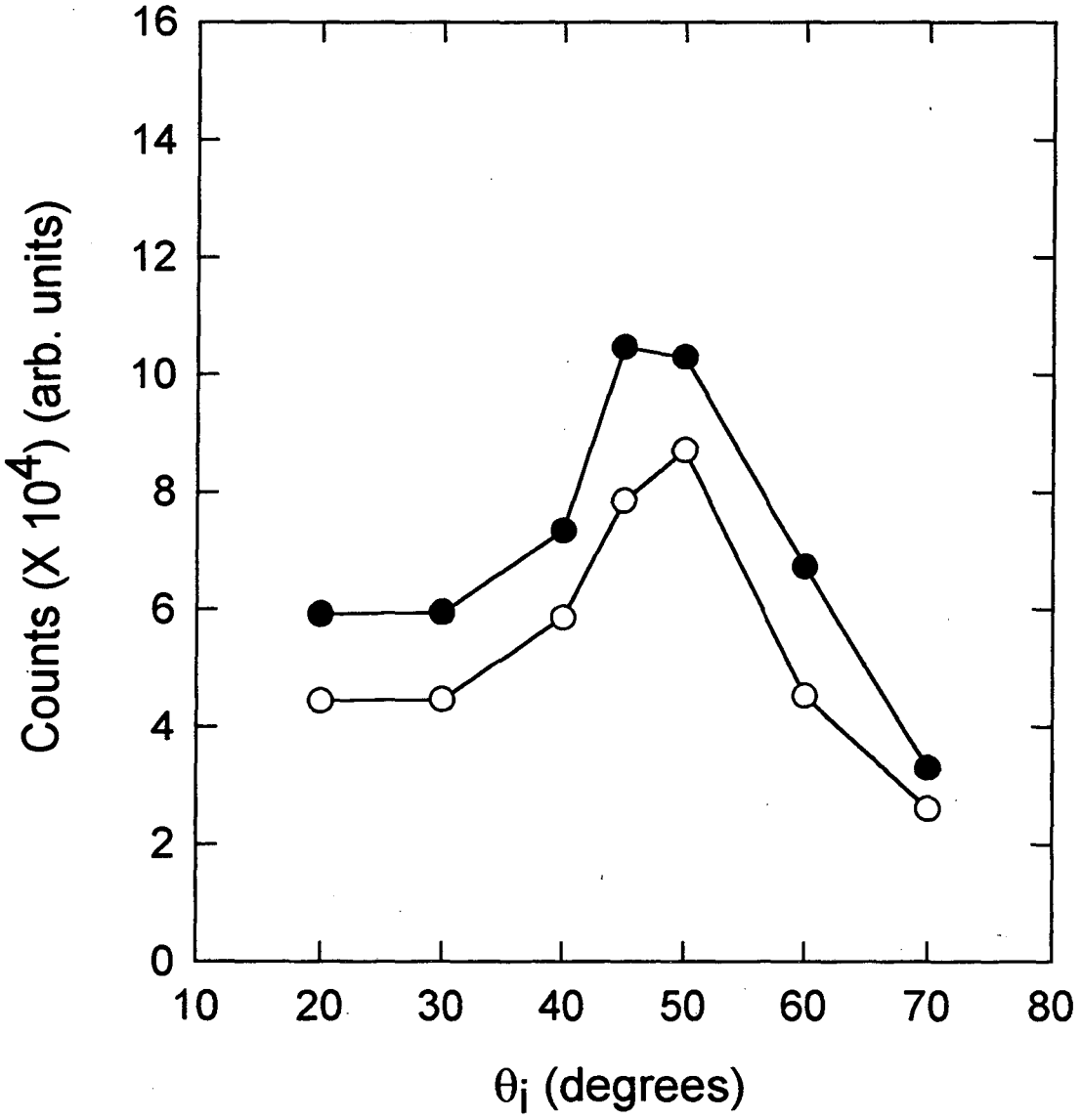


Fig. 7, L. A. Smoliar, J. Chem. Phys.

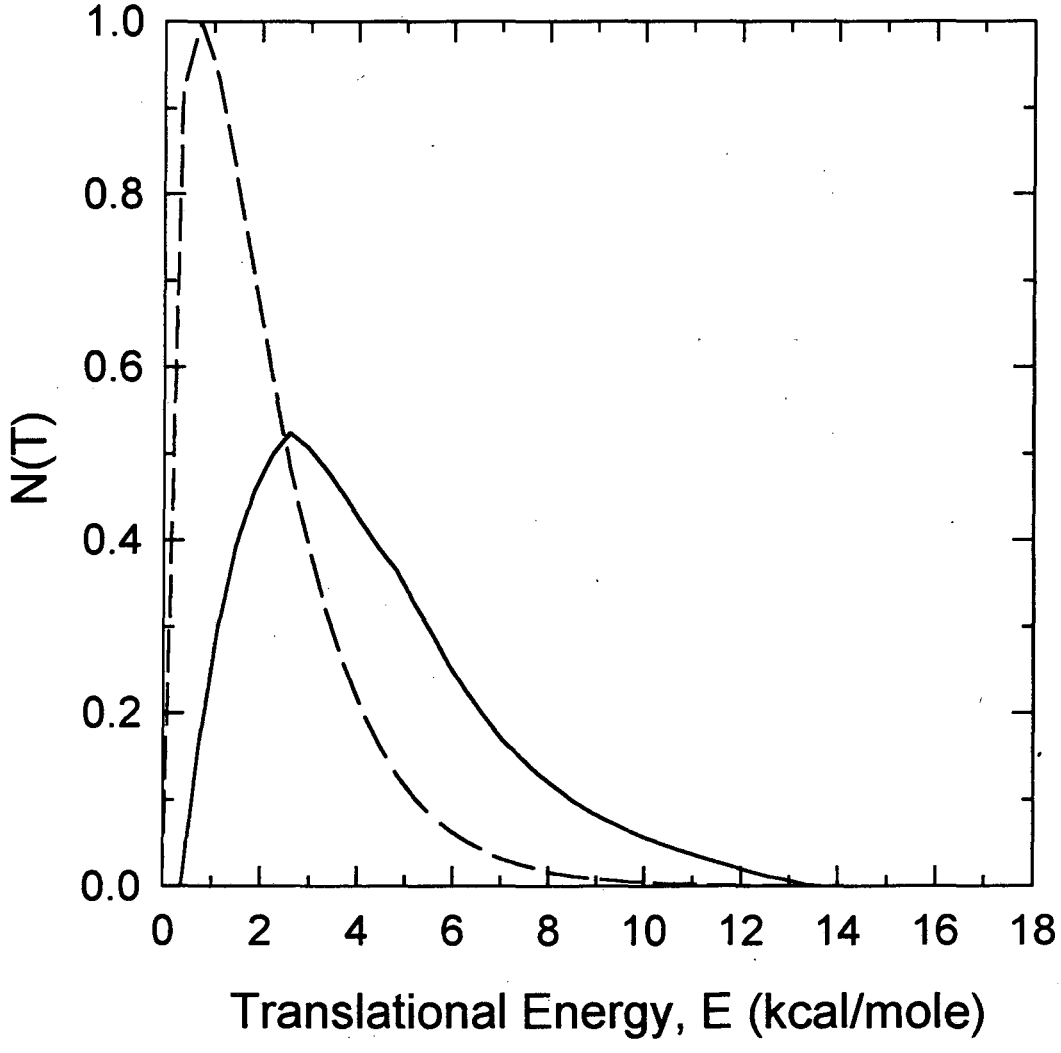
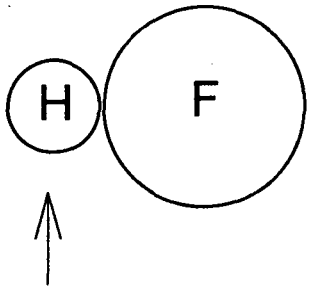
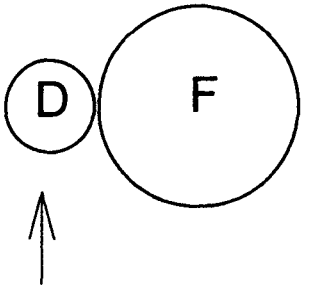


Fig. 8, L. A. Smoliar, J. Chem. Phys.



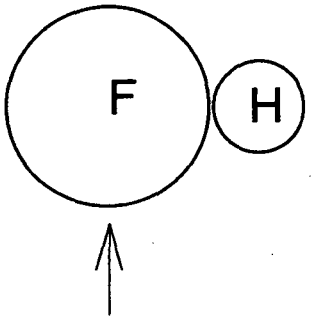
$$1/2\ M_H V_H^2 = 1/2\ M_{HF} V_{HF}^2$$

$$V_{HF}^2 = V_H^2 (M_H/M_{HF})$$



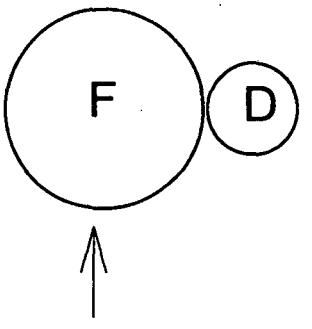
$$V_{DF}^2 = V_D^2 (M_D/M_{DF})$$

Expect 4X the Kinetic Energy



$$1/2\ M_F V_F^2 = 1/2\ M_{HF} V_{HF}^2$$

$$V_{HF}^2 = V_F^2 (M_F/M_{HF})$$



$$V_{DF}^2 = V_F^2 (M_F/M_{DF})$$

Expect the Same Kinetic Energy

Fig. 9, L. A. Smoliar, J. Chem. Phys.

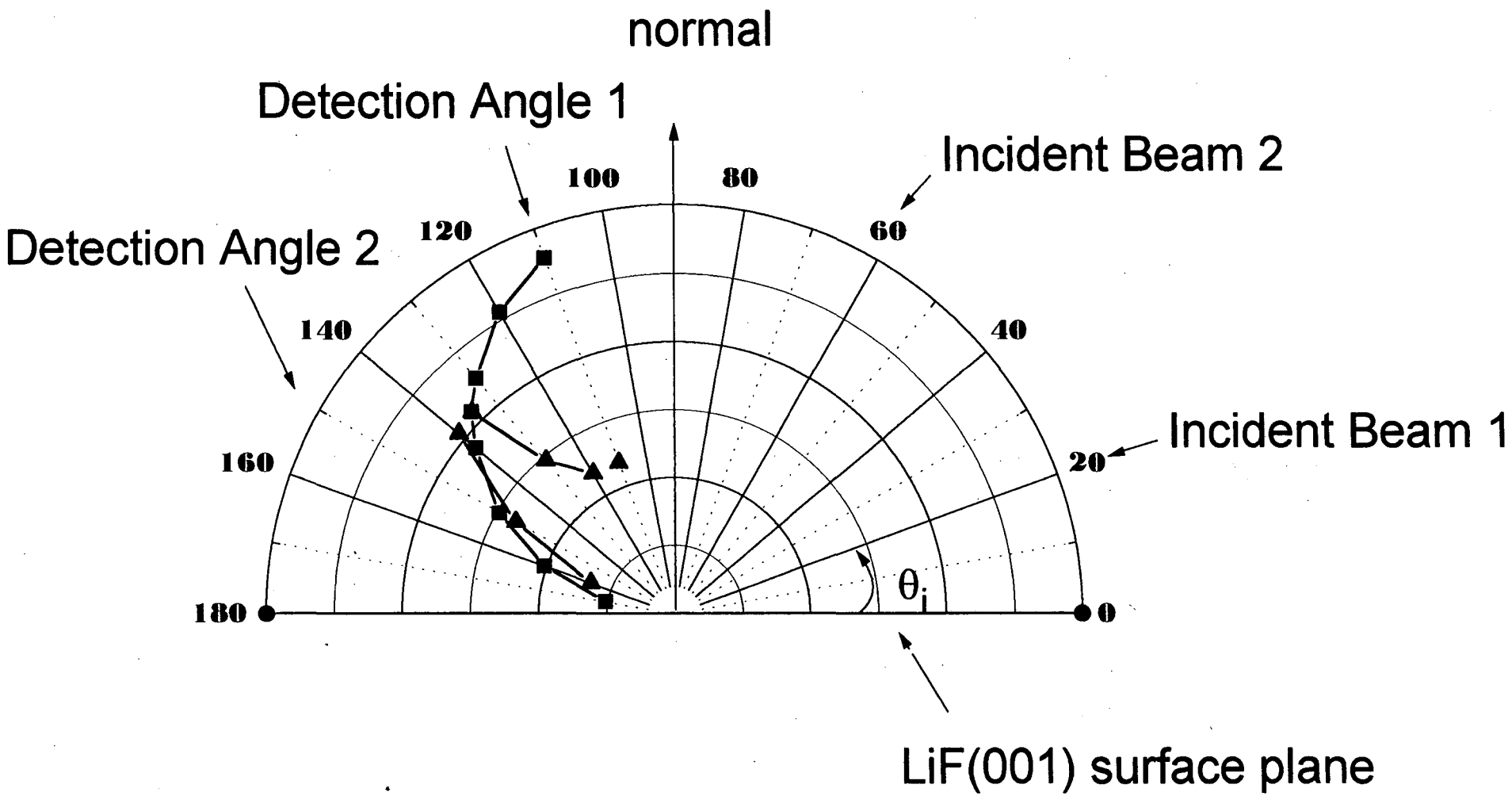


Fig. 10, L. A. Smoliar, J. Chem. Phys.

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