Elastic and rotationally inelastic diffraction of D₂ molecules from the LiF(001) surface

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More than 49 kinematically allowed elastic and rotationally inelastic diffraction peaks of D_2 molecules scattered from a 297 K single crystal LiF(001) surface have been detected in a high resolution scattering experiment for an incident beam energy of 85.3 meV (k_i =12.8 Å⁻¹) along the $\langle 100 \rangle$ and $\langle 110 \rangle$ azimuthal axes. This comprehensive data set has been collected with a new apparatus, described in some detail, with which high resolution (0.2°) angular distributions can be measured for a wide range of final angles for all incident angles between 0° and 90°. The relative rotational $j=0 \rightarrow 2$ and $1 \rightarrow 3$ transition probabilities for the specular peak approach 300%, but for rotational transitions associated with a first order diffraction peak the probabilities are typically less than 50% except for grazing incident angles, where a large resonant induced increase is observed. These results provide new evidence for a strong coupling of the rotational transitions to diffraction.

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I. INTRODUCTION

The scattering of molecules from single crystal surfaces provides a direct method to study the molecule-surface interaction potential and the role of the molecular internal degrees of freedom, which are basic prerequisites for the understanding of physisorption and chemisorption. Compared to atomsurface scattering, the scattering of molecules is experimentally more challenging due to the additional open inelastic channels. From the theoretical point of view, the understanding and the analysis of molecular scattering is also more demanding since the internal states and the anisotropy of the molecule must be accounted for. Thus much less theoretical and experimental work has been reported for the scattering of molecules than for the scattering of atoms.^{1,2}

The H_2 -LiF(001) system is the classical and historical example of molecular scattering from surfaces and today still serves as an important benchmark system for testing new calculation methods.^{3,4} Furthermore, the understanding of this relatively simple system can provide physical insight into more complicated systems such as the chemisorption interaction with reactive metal surfaces.⁵ After the pioneering reports of well-defined elastic diffraction of H₂ from LiF, NaCl, and NaF by Stern and co-workers in the early 1930s,^{6,7} comparable studies of the scattering of H₂ and D₂ from LiF were reported only much later in 1970 by O'Keefe et al.^{8,9} In both experiments elastic diffractive scattering and selective adsorption resonances (SAR) were observed. In their experiments O'Keefe et al. observed an increase in the unresolved background signal in going from He to H₂, and to D₂, which they attributed to rotational excitation of the molecules. Rotationally inelastic diffraction (RID), in which the translational energy of the molecule is transformed into rotational energy of the molecule or vice versa, was first resolved in angular distributions for H₂, HD, and D₂ from MgO by Rowe et al.^{10,11} and subsequently in a more extensive experimental and theoretical study of H₂ from LiF(001) by Boato et al.¹² Later, Kolodney et al.¹³ compared the incident energy dependence of the elastic diffractive scattering of He and H₂ from MgO(001). Subsequent time-of-flight (TOF) studies of D_2 and H_2 scattering from LiF(001) by Allison *et al.* were interpreted as indicating that rotational transitions of D_2 and H_2 on LiF(001) are dissipative and involve the phonons of the surface rather than being elastic diffractive.¹⁴ Brusdeylins *et al.* indicated, on the basis of extensive high resolution TOF analysis of D_2 from NaF, that both phonon excitations and rotational transitions occur simultaneously.¹⁵ Subsequently, Brusdeylins *et al.* reported an empirical fit potential for the interaction of D_2 with LiF(001) surface.¹⁶ Recently, Bertino *et al.* reported angular distributions of H_2 from LiF, which revealed a large difference between the diffractive scattering of normal- and para-H₂ (Ref. 17) confirming earlier predictions.^{18,19}

The first theoretical study of rotational transitions was reported by Logan²⁰ who used a simple quantum mechanical treatment for a rigid-rotor molecule. The reflection of a prolated ellipsoid from a flat surface was subsequently studied by Halbritter.²¹ With the advances in theoretical understanding, and computational techniques, various more sophisticated quantum mechanical methods have been introduced: Goodman et al. applied the CCGM (Cabrera, Celli, Goodman, and Manson) method²² to molecule scattering.²³ Garibaldi et al. extended the Eikonal approximation for scattering from a hard corrugated surface²⁴ to the scattering of H₂ and HD from LiF(001).²⁵ Close-coupling (CC) calculations of the scattering of hydrogenic molecules were first made by Wolken^{26,27} and later by Drolshagen et al.²⁸ and Brusdeylins et al.¹⁶ Gerber et al. investigated the scattering of H₂-LiF(001) for relatively high impact energies using the sudden approximation.²⁹ Recently, a time-dependent Hartree method was applied to H_2 -LiF(001) by Capellini *et al.*³ and also by Ehara et al.⁴ Several theoretical studies have been devoted to the question of the coupling between the parallel momentum transfer accompanying diffraction and rotational transition.28,30-32

In the theoretical calculations up to 1985 mentioned above, the magnetic quantum number transitions in the scattering and rotational state transitions are either neglected or only considered in first order approximation. Moreover, the interaction between the molecular quadrupole and the elec-

trostatic field of the surface ions is also neglected. The hard corrugated wall approximation²⁵ used up to that time is only valid for low corrugations and potential well depths and has the additional disadvantage that the electrostatic interaction term cannot be represented explicitly in the interaction potential. In the usual close-coupling calculations the model potentials are independent of the azimuthal angle of the molecular orientation, and thereby the Δm_i transitions are not allowed.²⁶⁻²⁸ Furthermore, Boato et al., without a detailed analysis, concluded from their experimental results that m_i is approximately conserved.¹² However, the 1979 calculations by Hill³³ revealed that the rotational transitions for H₂ -LiF(001) are strongly affected by the interaction between the molecular quadrupole moment and the electric field of the ions at the crystal surface which can cause a reorientation of the molecules thereby leading to Δm_i transitions. Subsequent extensive calculations of Kroes and his coworkers published in 1995 and 1998 based on the close-coupling wave packet (CCWP) method with a realistic interaction potential demonstrate that the quadrupole-electrostatic interaction does contribute significantly to the scattering probabilities and, moreover, that m_i transitions make a large contribution.^{18,19} Experimental supporting evidence comes from the observation of large differences in the diffraction peak intensities of molecular beams of *n*- and p-H₂.¹⁷ A very recent comparative experimental and theoretical study of H₂-NaCl scattering reveals that the Δm_i transitions couple preferentially to the shear horizontal modes which in inelastic scattering of He atoms is symmetry forbidden.³⁴

Compared to H_2 , the D_2 -LiF(001) system studied here has a number of experimental as well as theoretical advantages. Rotational transitions of D_2 are expected to be more probable than for H₂, since the rotational energy levels are more closely spaced in D_2 . Therefore the coupling of the diffractive and rotational transitions can be studied in D_2 at thermal collision energies for which only a few rotational transitions of H₂ are barely observed. Moreover, D₂ provides a much greater dynamical range of the scattering signals than H₂, since the detector background signal at mass 4 amu (D_2^+) is lower by several orders of magnitude than at mass 2 amu (H_2^+) . Since the interaction potentials are identical, a comparison of H_2 and D_2 is expected to provide deeper insight into the scattering of molecules from alkali halide surfaces via the different masses and rotational energy levels of the projectiles.

The present experiments are carried out with a new apparatus which makes it possible to cover a wide range of final angles for each incident scattering angle. Previously most of the surface scattering experiments carried out in Göttingen used a fixed-angle setup^{35–38} in which the source-to-detector angle (θ_{SD}) is fixed and the crystal polar and azimuthal angles are varied by rotating the target. This relative simplicity makes it possible to install several differential pumping stages preceding the detector in order to achieve high signalto-background ratios, allowing the detection of the low inelastic signals from surface phonons.³⁹ The major disadvantage of the fixed angle setup is that the incident and final scattering angles θ_i and θ_f (defined with respect to the surface normal), respectively, are coupled by the relationship $\theta_i + \theta_f = \theta_{SD}$ and cannot be varied independently of each other. Direct comparisons with theory, which for a specified incident angle provides diffraction peak intensities for all final angles, are therefore limited. The more traditional rotatabledetector setup, on the other hand, overcomes the problems mentioned above.⁴⁰⁻⁴² However, in the commonly used construction the detector is mounted close to the sample inside the sample vacuum chamber in order to simplify the detector rotation mechanism, making, however, differential pumping of the detector virtually impossible. Thus the angular and TOF resolutions and signal-to-background ratio of this setup are usually rather low. In the setup used here the detector arm also has several differential pumping stages as with the fixed-angle setup but can be rotated, so that this new apparatus combines both the advantages of the fixed-angle and rotatable-detector setups. This feature, combined with its high angular resolution and favorable signal-to-background ratio, allows a wide range of new experiments in molecular and atomic beam scattering. A similar construction was first used previously in an apparatus (HUGO) in our institute by Lilienkamp et al.43 but was abandoned in later experiments because of stability problems. Another similar construction is a rotatable-source setup which also is cumbersome since the large source chamber with its high-throughput pumps needs to be rotated.⁴⁴

In this paper the results of angular distribution measurements of D₂ molecules scattered from LiF(001) over a wide range of incident and final angles at a constant incident beam energy of 85.3 meV (k_i =12.8 Å⁻¹) and a surface temperature of 297 K along both symmetry axes are presented. The high angular resolution and favorable signal-to-background ratio make it possible to detect virtually all the elastic diffraction and RID peaks.

The paper is organized as follows. In Sec. II the apparatus is described in detail. In Sec. III the kinematics of the molecular scattering from surfaces and some experimental aspects are discussed. Measurements of angular distributions are then presented in Sec. IV with particular attention to the aspects relevant for the data evaluation. Next, in Sec. V, the procedure for extracting the intensity profiles for a constant incident angle from fixed-total angular scans is described and some of the equations needed for a theoretical comparison are provided. The thermal attenuation of peak intensities is presented in Sec. VI. Finally, in Sec. VII the experimental results are presented and discussed. The paper closes with a summary and outlook in Sec. VIII.

II. APPARATUS

A schematic diagram of the apparatus, which is described in detail in Ref. 45, is shown in Fig. 1. Figure 2 shows a top view of the actual apparatus and provides an overview of some of the technical details and the components as well as the distances between the source and the target and the radius of the circular track on which the detector chamber was mounted. Briefly, the beam is generated in the source chamber by skimming the core of a supersonic free jet expansion. The skimmed beam travels first through the differential pumping stage-1 (DPS-1) and the differentially pumped



FIG. 1. A schematic diagram showing the functional units of the apparatus and the definitions of the scattering angles.

chopper chamber before it is scattered from the crystal surface in the target chamber. After passing through four additional differential pumping stages along the 1.6 m long time-of-flight tube the scattered beam particles reach the detector where they are ionized by electron bombardment and the fragment ions are selected by a magnetic mass spectrometer and registered by a channeltron multiplier.⁴⁶ The pumping stages, the collimation of the beam path, and the vacuum conditions in various chambers are summarized in Table I.

A circular rail provides for total angles from $\theta_{SD} = 40^{\circ}$ to 190° measured with respect to the incident beam about a vertical axis through the center of the target chamber. The target chamber is also mounted on a rotatable central base to provide access of the incident beam through one of seven possible beam entrance ports on the target chamber at intervals of 22.5°. On the beam exit side of the target a reentrant bellows connection allows varying the detector angle over an angular range of $\pm 12^{\circ}$ through a spindle driven by a stepping motor fixed on the circular track. The angle θ_{SD} is measured by an encoder mounted on the rotational center of the detector arm. To change θ_{SD} to cover the next angular range of ±12° fixed by a specified beam entrance port, the beam entrance port is disconnected and the chopper chamber is vented. The target chamber and the stepping motor base (No. 21 in Fig. 2) are also disconnected and the target chamber together with the detector arm is moved to a new position



FIG. 2. A scaled top-view diagram of the molecular beam apparatus. The beam is produced in the source (not shown) mounted in the source chamber (1), then passes through the skimmer (2) and the first differential pumping stage (DPS-1) (3). It is chopped into short pulses by the chopper (4) in the next chamber (5). Its divergence is defined by the iris (6). Through one of the seven beam entrance ports (7) it enters the target chamber and is scattered by the target (8). The scattered molecules pass through a differential pumping stage, (DPS-2) (9), the time-of-flight tube (10), the DPS-3 (11) and two additional compact differential pumping stages, (12), before reaching the detector chamber (13). The electron-impact ionized molecules are mass selected by an electromagnet (14) and detected by a channeltron (15). All the chambers following the target chamber are mounted on a pair of linear rails (16). The flight distance can be changed within the range provided by the bellows (17). The whole apparatus is built on a massive main supporting frame (18). The detector arm is mounted on a circular track (19) with a radius of 1.6 m. The detector arm is rotated by a driving rod (20) and a stepping motor (21). The detector arm can be rotated by $\pm 12^{\circ}$ enabled by reentrant bellows (22). The sample is inserted through the window flange (23) into the target chamber.

TABLE I. Beam collimation, chambers, and dimensions of the apparatus. The dimensions of the collimators denote the diameters of circular apertures and for the detector, the effective size of the ionization region in rectangular width \times height \times length. The positions are given with respect to the skimmer tip. The UHV pumps are for the chambers preceding the given collimating apertures in the same row.

Collimation	Dimensions (mm)	Position (mm)	UHV pump [Pumping speed (He) (L s ⁻¹)]	Typical background pressures (mbar)	Typical working pressures (mbar)
Nozzle	10 µm	-7.5		0 bar	120 bar
Skimmer	400 µm	0	Balzers TPH 2200 S [3200]	1×10^{-7}	1×10^{-3}
Aperture	4.1	300	Leybold Turbovac 361 [380]	6×10^{-8}	7×10^{-5}
Chopper		550			
Iris	2.5	1132			
Aperture	6	1260	Leybold Turbovac 361 [380]	3×10^{-8}	2×10^{-7}
Target	10×10	1500			
Aperture	6.7	1670	Leybold Turbovac 361 [380]	8×10^{-9}	3×10^{-8}
Aperture	6.7	1870	Leybold Hy.Cone 200 [180]		
Aperture	6.7	2080	Pfeiffer TPU 062 [56]		
Aperture	6.7	2316	Pfeiffer TMU 065 [32]	2×10^{-10}	3×10^{-9}
Aperture	6.7	2504	Pfeiffer TMU 065 [32]		
Detector	$4.6 \times 6.6 \times 4.6$	2816	Pfeiffer TMU 260 [220]	1×10^{-10}	7×10^{-9}

with a new beam entrance port and, subsequently, the vented chamber is pumped down.

The vacuum requirements in the vented chamber depend on the crystal to be investigated. As LiF(001) crystals are rather inert and can be investigated even under poor vacuum conditions, a total pressure of 10^{-7} mbar in the chopper chamber, leading to a sufficient total pressure of 10^{-8} mbar in the target chamber, can be reached within 1 h and a new series of experiments can be started. With this procedure, any total angle between $\theta_{SD}=40^{\circ}-190^{\circ}$ can be accessed.

The incident beam angular collimation is defined by a circular aperture in the iris chamber with an adjustable diameter of 0.8 – 5.0 mm. In the present experiments an iris diameter of 2.5 mm is used, which leads to an incident beam divergence of $\Delta\theta$ [full width at half maximum(FWHM)] =0.12°. In most of the experiments reported here θ_{SD} is first set at a given angle and the incident and final angles, θ_i and θ_f , are changed by rotating the crystal holder with a stepping motor and the angle is measured with an independent angular encoder. A CAMAC interface controls the translational and angular adjustment of the crystal position as well as the angles θ_i and θ_{SD} and supervises the data accumulation via a personal computer.

Time-of-flight (TOF) measurements are used to analyze the translational energy of both the incident and scattered beams. The beam is chopped by a 0.1 mm thick, 138 mm diameter metal disk with two identical equilateral trapezoid slits of height of 15 mm and of widths of 1 mm at the bottom and 5 mm at the top. By moving the entire chopper assembly in and out of the beam the effective width of the slit can be adjusted. The ball bearing-supported chopper operates in the range of 75–500 Hz. The total flight time of the chopped beam pulse from the chopper to the detector is measured with a time-to-amplitude converter. In the present study, the TOF method is used to determine the incident beam velocity and to identify a few unclear RID and elastic diffraction peaks. The relatively expensive D_2 gas is recycled. The recycling unit consists of a series of oil filters and two Al_2O_3 filters cooled with liquid nitrogen following the source chamber forevacuum pump and separates the recycled D_2 gas from oil and gaseous contaminants. After the purification stage the gas pressure is raised up to 130 bar by a two-stage compressor.⁴⁷ A cold trap with a 10 μ m filter provides for a final filtering stage for both He and D_2 before the nozzle. Since the amount of the gas circulating in the system is relatively large in comparison to the losses mainly via the skimmer, the system can run on D_2 for more than a week without a partial refill.

All experiments are carried out with n-D₂ (Ref. 48) expanded through a 10 μ m orifice from a stagnation pressure of 120 bar and a temperature 300 K. For n-D₂ the room temperature equilibrium statistical weights of para-D₂ (odd *j*) and ortho-D₂ (even *j*) are 1/3 and 2/3, respectively. Previous investigations demonstrated that in the expanded molecular beam the occupation of the rotational states of the molecules show a nearly Boltzmann distribution and the rotational distributions can be characterized by an effective rotational temperature T_R , which can be expressed with an empirical fit for n-D₂ as⁴⁹

$$\log(T_R/T_0) = -0.40 \log[P_0 d \cdot T_{ref}/T_0] + 0.16, \qquad (1)$$

where T_{ref} =293 K is a reference temperature and P_0d is given in units of torr cm. Thus in the present experiments, the rotational temperature is estimated to be 72 K. The corresponding fractional populations of the rotational levels are listed in Table II. From TOF measurements the beam energy is found to be E_i =85.3 meV (k_i =12.8 Å⁻¹) with a FWHM of $\Delta E_i/E_i$ =7.9%. TABLE II. The properties of the n-D₂ beam used in the present experiments and the energies of some relevant rotational and vibrational excitations (Ref. 84).

Source conditions:	<i>T</i> ₀ =300 K
	$P_0 = 120 \text{ bar}$
	$d=10 \ \mu m$ (nominal diameter)
Incident beam:	$k_i = 12.8 \text{ Å}^{-1}$
	$E_i = 85.3 \text{ meV}$
	$\Delta E_i / E_i (\text{FWHM}) = 7.9\%$
	T_{rot} =72 K
Rotational distributions:	$n(j_i=0)=58\%$
	$n(j_i=1)=33\%$
	$n(j_i=2)=8\%$
Transition energies:	$\Delta E_{rot}(0 \rightarrow 2) = 22.2 \text{ meV}$
	$\Delta E_{rot}(1 \rightarrow 3) = 36.9 \text{ meV}$
	$\Delta E_{rot}(2 \rightarrow 4) = 51.4 \text{ meV}$
	$\Delta E_{vib}(0 \rightarrow 1) = 386 \text{ meV}$

The LiF crystals⁵⁰ are cleaved in air into 3 to 4 mm thick slices from larger slabs of cross-section of $10 \times 10 \text{ mm}^2$ and mounted in the vacuum chamber within about 5 min. The cleavage results in highly clean and atomically flat surfaces with large terraces^{51–55} so that scattering experiments could be performed immediately without any further treatment under UHV conditions at room temperature. To reduce the effect of the low concentration of defects resulting from the cleavage,^{56–58} the crystals are annealed for 15 h at 800 K. In most of the present experiments the surface temperature is T_s =297 K.

III. KINEMATICS

The positions of the elastic diffraction and RID peaks are defined by the kinematical conditions

$$\mathbf{K}_f - \mathbf{K}_i = \Delta \mathbf{K} = \mathbf{G}_{mn},\tag{2}$$

$$E_{f} - E_{i} = \frac{\hbar^{2}}{2m}k_{f}^{2} - \frac{\hbar^{2}}{2m}k_{i}^{2} = \Delta E_{rot},$$
(3)

where \mathbf{K}_i and \mathbf{K}_f are, respectively, the parallel components of the incident and outgoing wave vectors $(\mathbf{k}_i, \mathbf{k}_f)$ of the particles with mass m, E_i and E_f are initial and final energies of the molecules, and \mathbf{G}_{mn} is the reciprocal lattice vector given by

$$\mathbf{G}_{mn} = \left(\frac{2\pi}{a}m, \frac{2\pi}{a}n\right),\tag{4}$$

where a=2.847 Å is the lattice constant of the LiF(001) surface. ΔE_{rot} is the difference between the energies of the initial and final quantum levels of the rotational transition: $(j_i \rightarrow j_f)$. Typical values of ΔE_{rot} are listed in Table II. Since the energy of the first excited vibrational state of D₂ is 386 meV, vibrational excitation at the beam energies of 85.3 meV used here is not energetically accessible and therefore not observed in the present experiments.



FIG. 3. Typical angular scan lines and the kinematical conditions of the major observed peaks for initial and final angles for D₂-LiF(001) with an incident beam wave vector of $k_i = 12.8 \text{ Å}^{-1}$ $(E_i = 85.3 \text{ meV})$ along the $\langle 100 \rangle$ direction. For illustration constant- θ_{SD} incident angular scan lines are shown for $\theta_{SD} = 57.5^{\circ}$, 90°, and 168.5° (short-dotted lines) and a constant- θ_i angular scan line is shown for $\theta_i = 40^\circ$ (short-dashed line). (mn: $j_i j_f$) represents the RID peak for a transition from an initial rotational state j_i to a final rotational state j_f coupled with the diffraction peak (mn). Continuous lines: elastic diffraction peaks, dashed lines: $(0 \rightarrow 2)$ RID peaks, dotted lines: $(1 \rightarrow 3)$ RID peaks, and dashed-dotted lines: $(2 \rightarrow 0)$ RID peaks. Note that all RID peaks merge with their elastic peaks at low incident angles. Moreover, rotational transitions to higher rotational states lie at lower incident angles with respect to their elastic peaks. The (m,n) and (-m,-n) peaks are symmetric with respect to the specular peak. The incident beam, I_0 is at $\theta_i = \theta_f = 90^\circ$.

There are several possible ways in which diffraction patterns in surface scattering can be measured with the present apparatus. These possibilities can best be illustrated with a two-dimensional diagram spanning the space of all possible incident and final angles shown in Fig. 3. The figure also shows the angular positions of elastic diffraction and RID peaks defined by kinematical conditions given in Eqs. (2) and (3) for the $\langle 100 \rangle$ direction at a collision energy of 85.3 meV. Following the notation given above, the elastic diffraction peaks are denoted as (mn) and the inelastic peaks due to a rotational transition $(j_i \rightarrow j_f)$ are denoted as $(mn:j_ij_f)$. In Fig. 3 the specular peak, for instance, corresponding to (00), is a diagonal straight line going from the bottom left- to the upper right-hand corner. The elastic diffraction peaks of the same order, indicated by the continuous line curves, but with negative and positive signs of m and nare symmetric with respect to the specular peak diagonal.

In the experimental strategy used here for exploring the peak intensities in this angular space (θ_i, θ_f) , the total angle (θ_{SD}) is fixed and the incident angle (θ_i) and final angle $(\theta_f = \theta_{SD} - \theta_i)$ are changed by rotating the target. In the (θ_i, θ_f) space, in Fig. 3, such constant- θ_{SD} scan lines are straight lines extending from the upper left to the bottom right which

intersect the specular peak at right angles. Scan lines for θ_{SD} =57.5°, 90° and 168.5° are shown as examples. In the previous fixed-angle setups θ_{SD} was usually fixed at θ_{SD} =90°. Since with the new apparatus θ_{SD} scans can be made for all angles between θ_{SD} =40° and 180°, about 90% of the total (θ_i , θ_f) space can be covered.

Another possible experimental strategy is to fix θ_i (or θ_j) and scan θ_j (or θ_i). A typical fixed incident angle scan line is illustrated in Fig. 3 by a vertical line for θ_i =40°. In this case the detector is rotated while keeping the incident angle constant which provides the intensities of all elastic and/or RID peaks for a given incident angle. However, in the present setup, the rotation of the detector arm is too slow and it is necessary to break the vacuum and change the beam ports several times in order to cover the entire angular range. Thus it would have taken several days to get one scan for a constant incident angle, whereas a constant- θ_{SD} scan takes only about 15–20 min since only the crystal is rotated.

Even under these conditions with the angular resolution of 0.12° it would have been necessary in order to access all the available information in the entire accessible (θ_i, θ_f) space, to increase θ_{SD} in increments of about 0.1°, i.e., less than the half-width of the sharpest peak, and at each θ_{SD} to take an angular scan by rotating the crystal. This would have required 1800 angular scans with roughly 900 data points per scan corresponding to a huge matrix of intensity $[\theta_i, \theta_{SD}]$, which if converted to the intensity matrix $[\theta_i, \theta_f]$, would, thereby, provide a complete picture of the scattering process from the surface for virtually all initial and final angles. Aside from the complications arising from the administration of this large amount of data, an important consideration is the long time of the order of weeks of continuous measurement required for such an experiment. Although our apparatus had a high stability and good reliability, it is impossible to rule out over such a long time of operation some instabilities such as in the operation of the source or detector and in the mechanical alignment, which may have even had accumulative effects and thereby spoil the "coherence" of the results.

Therefore the following easier and more economical method, which also provides the same complete picture, albeit with somewhat less detail, was adopted. Incident angular scans at constant detector angles are measured in the limited range between θ_{SD} =57.5° and 168.5° with relatively large angular steps of $3^{\circ}-5^{\circ}$. Since the peak intensities do not change appreciably with θ_{SD} , the intensities of all the expected peaks are obtained over a wide range of incident and final angles (see Fig. 3). The peak intensities for all peaks at a constant incident angle are then obtained by an interpolation of the incident angle intensity plot. This is a reasonable method provided that the peak intensities change slowly and do not exhibit strong resonant features. With this threedimensional representation of the data the development of the intensity of a certain peak with any of the desired angles can be traced out and analyzed or alternatively, the intensities of the peaks at a constant incident angle can be extracted for comparison with theoretical calculations. This procedure is illustrated in Fig. 4 where four different measured total-angle scans are presented in a three-dimensional plot as functions of initial and final angles. The observed peaks can be identified with the aid of Fig. 3.



FIG. 4. For illustration of Fig. 3, measured incident angular scans are shown at four different constant total angles of $\theta_{SD} = 57.5^{\circ}$, 118°, 150°, and 168.5° for D₂-LiF(001) along the $\langle 100 \rangle$ direction. $P_0=120$ bar and $T_0=300$ K. $E_i=85.3$ meV and $k_i = 12.8$ Å⁻¹. The diagonal lines show the projections of the scans on the $[\theta_i, \theta_f]$ plane.

IV. CONSTANT-TOTAL ANGLE SCANS

Typical angular scans for a constant total scattering angle of θ_{SD} =90° are illustrated in Figs. 5 and 6 for the $\langle 100 \rangle$ and $\langle 110 \rangle$ scattering directions. Each angular scan was carried out with incident angular steps of 0.05°. Integration times of 0.5 s were used to measure the signal at each angular step. In the $\langle 100 \rangle$ direction 17 distinct peaks are clearly resolved and several more appear as shoulders. In the $\langle 110 \rangle$ direction up to 27 peaks can be observed. The greater density of the peaks in the $\langle 110 \rangle$ direction is due to the smaller reciprocal lattice vector **G** and for this reason also the overlapping of peaks is more likely. Nevertheless all the peaks can be identified with the aid of the kinematical conditions in Eqs. (2) and (3) as due to either elastic diffraction or RID peaks. The identifica-



FIG. 5. One of the best of several incident angular scans for D₂-LiF(001) along the $\langle 100 \rangle$ direction. $T_s = 130$ K, $T_0 = 300$ K, and $P_0 = 120$ bar. $E_i = 85.3$ meV ($k_i = 12.8$ Å⁻¹) and $\theta_{SD} = 90^{\circ}$.



FIG. 6. One of the best of several incident angular scans for D₂-LiF(001) along the $\langle 110 \rangle$ direction. $T_s = 130$ K, $T_0 = 300$ K, and $P_0 = 120$ bar. $E_i = 85.3$ meV ($k_i = 12.8$ Å⁻¹) and $\theta_{SD} = 90^{\circ}$.

tion of the peaks in the angular scans is facilitated by the symmetry of the elastic diffraction peaks of plus and minus order with respect to the specular peak (see Fig. 3). The inelastic peaks for excitation to higher rotational levels lie at lower incident angles with respect to their parent elastic peaks and at higher angles for deexcitation. Either Eqs. (2) and (3) or Fig. 3 can be used to identify overlapping peaks. For instance, the peaks (00:20) and (-1-1:13) and the peaks (33) and (22:13) are at the same angles for the $\theta_{SD} = 90^{\circ}$ -scan line so that the peaks observed at about 48° and 14° in Fig. 5 can each be attributed to two overlapping peaks. In angular distributions, as seen in Figs. 5 and 6 in both scattering directions, most of the inelastic peaks are due to excitations from the predominantly populated $j_i=0$ and 1 rotational states. In addition, some $(2 \rightarrow 0)$ deexcitation rotational transitions are also observed. Since the fractional population of the $j_i=2$ level in the incident beam is only about 8% at the given stagnation conditions, the deexcitation peak intensities are low, but the transition probabilities are comparable with the transition probabilities of $(0 \rightarrow 2)$ and $(1 \rightarrow 3)$.

It is also seen that there are large differences in the widths of the peaks in both Figs. 5 and 6. Some peaks such as the (-1-1:02) and (11:20) in Fig. 5 and the (-20:13) in Fig. 6 are as sharp as the specular peak. This can be understood by examining the incident wave vector dependence of the incident angles for some typical elastic and RID peaks as illustrated in Fig. 7. For example, the position of the (-1 - 1:02) peak is almost independent of the incident wave vector for k_i greater than about 9 Å⁻¹. Thus, despite the inherent energy spread of the incident beam, these peaks appear to be very sharp. We designate this effect, which was first discovered in 1975¹¹ and later confirmed at higher resolution,¹⁵ as *kinematic rotational focusing*. A related effect, called kinematical focusing, is also found for surface phonon excitations.⁵⁹

In Figs. 8 and 9 all the measured angular scans are presented for each of the two azimuthal directions. As expected from Fig. 3 the angular ranges for small θ_{SD} are restricted to the region of small incident angles and increase with increasing θ_{SD} up to $\theta_{SD}=90^\circ$, where the range extends from θ_i



FIG. 7. Wave vector dependence of the incident angle of the elastic (solid lines) and $(0 \rightarrow 2)$ inelastic (dashed lines) peaks for D₂-LiF(001) along the $\langle 100 \rangle$ where $\theta_{SD}=90^{\circ}$. The peak widths, $\Delta \theta_i$, of the (-1-1) diffraction peak and its RID peak are illustrated for the case of a finite beam energy spread of Δk_i . Note that the inelastic peak (-1-1:02) is narrower than the elastic diffraction peak (-1-1) because the inelastic peak depends very little on the incident wave vector.

=0° to 90°. For $\theta_{SD} > 90^\circ$ the angular range narrows again and the distributions are shifted to the region of large incident angles. The number of observed peaks decreases approximately with increasing θ_{SD} and beyond 150° and 160° in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, respectively, the patterns consist of only the specular peak. Although some RID peaks as, for example, the (-1-1:13) peak (see Fig. 3), are kinematically possible at the highest detector angle in both directions, they are not observed due to the overlapping of peaks and probably due to their low transition probabilities. At low θ_{SD} the RID peaks associated with the (-2-2), (-3-3), and (-30) diffraction peaks merge with the elastic peaks as clearly seen in Fig. 3. The reason is that the molecules scattered with large minus G vectors rebound from the surface in a direction almost perpendicular to the surface $(\theta_f \approx 0^\circ)$. Since they move nearly normal to the surface, the change in their velocity accompanying a rotational transition does not have a significant effect on the final angle.

The broad inelastic background of typically 10^4 counts/s seen in the angular scans in Figs. 8 and 9 is especially noteworthy. The background measured with He scattering from the LiF surface is typically two orders of magnitude less than the present background.^{45,60} Similarly, large background signals have not been observed for H₂ scattering from LiF(001).^{17,61} Thus it appears unlikely that the large background is due to defects. One possible explanation is the existence of low-lying rotational energy levels creates more open channels for the phonon excitations, contributing to a larger inelastic background.

V. EVALUATION OF PEAK INTENSITIES

In order to obtain the transition probabilities the influences of the instrumental broadening, finite crystal tempera-



FIG. 8. A series of consecutively measured incident angular scans at different total angles for D₂-LiF(001) along the $\langle 100 \rangle$ direction (ϕ =45°). T_s =297 K, P_0 =120 bar, and T_0 =300 K. E_i =85.3 meV and k_i =12.8 Å⁻¹. The legend of the rotational transitions ($j_i \rightarrow j_f$): **a** denotes (0 \rightarrow 2), **b** denotes (1 \rightarrow 3), and **c** denotes (2 \rightarrow 0). Integer numbers indicate diffraction orders m=n. The corresponding final angles for each scan can be obtained from the relationship $\theta_f = \theta_{SD} - \theta_i$.



FIG. 9. A series of consecutively measured incident angular scans at different total angles for D₂-LiF(001) along the $\langle 110 \rangle$ direction (ϕ =45°). T_s =297 K, P_0 =120 bar, and T_0 =300 K. E_i =85.3 meV and k_i =12.8 Å⁻¹. Integer numbers indicate diffraction orders (m,0).

ture, the energy spread of the beam, and of the initial distributions of the internal states on the experimental intensities must be accounted for. As discussed in the previous section, the peaks have quite different intensities and widths depending on the incident beam energy and the scattering angles θ_i , θ_f , and θ_{SD} .³⁷ Explicit corrections for the instrumental resolution and the finite velocity spread of incident beam energies are a very time-consuming procedure. In order to circumvent this, a better measure of the experimental intensities is provided by the areas instead of the heights of the peaks. This is a reasonable approximation so long as the beam divergence is kept constant and the scattering probabilities do not change significantly within the energy spread of the incident beam. The peak-area intensities of the elastic and RID transitions given below are obtained by Gaussian fitting after subtraction of the background.

The zero-temperature transition probability of an elastic or RID peak from an initial state j_i to a final rotational state j_f can then be calculated from the following expression:

$$P(mn:j_i j_f) = \left\lfloor \frac{I(mn:j_i j_f)}{I_0 \cdot n(j_i) \cdot \eta(\theta_i)} \right\rfloor \sqrt{\frac{E_i + \Delta E_{rot}}{E_i}} \\ \times \exp[2W_{mn:j_i j_f}(\theta_i, E_i, E_f, T_s)],$$
(5)

where $I(mn:j_i j_f)$ is the peak-area integrated intensity of molecules scattered from a crystal of finite surface temperature of T_s . I_0 is the peak-area intensity of the incident beam which is measured at θ_{SD} =180°. $n(j_i)$ is the fractional population of the rotational state j_i in the incident beam. The geometrical factor $\eta(\theta_i)$ accounts for the possibility that at large incident angles the area of the target projected onto the direction of the incident beam can be smaller than the area of the incident beam. The square root term corrects for the inverse proportionality of the electron impact ionization efficiency on the velocity of scattered molecules. The exponent in the third term has a positive sign to compensate for the thermal attenuation of the coherent intensities. W is the Debye-Waller factor defined by^{62,63}

$$W(T_s) = \frac{3\hbar^2 (k_{iz}' + k_{fz}')^2 T_s}{2Mk_b \Theta_D^2}.$$
 (6)

Here Θ_D is the surface Debye temperature, *M* is the average mass of the surface atom, and k'_{iz} and k'_{fz} are corrected surface normal components of the initial and final wave vectors, respectively. The Beeby correction⁶⁴

$$k_{i(f)z}' = \left[k_{i(f)z}^{2} + \frac{2mD}{\hbar^{2}} \right]^{1/2}$$
(7)

is used to account for the gain in perpendicular momentum of the incoming and outgoing particles of mass m in the attractive potential with a depth D.

For comparison with the theory it should be noted that, since the magnetic quantum numbers m_j in these experiments are not selected and their changes cannot be detected, Eq. (5) provides an experimental probability averaged over the magnetic quantum number (m_j) . The $P(mn: j_i j_f)$ values obtained from Eq. (5) are therefore related to the transition matrix element S by averaging over m_{j_i} and summing over m_{j_i} :

$$P(mn:j_i j_f) = \frac{1}{2j_i + 1} \sum_{m_{j_i}, m_{j_f}} |S[00, j_i m_{j_i} \to mn, j_f m_{j_f}]|^2.$$
(8)

Whereas the j_i and j_f levels associated with RID peaks are identified with the kinematical equations, this is not true for the elastic diffraction peaks which are averages over the rotational distribution in the incident beam and thus

$$P(mn) = \sum_{j_i} P(mn; j_i j_i) n(j_i).$$
(9)

Although these quantities can be used for a comparison with theory, it is more advantageous to use the ratios of the probabilities. To compare a RID peak with the associated elastic peak (m,n) the following ratio is used:^{17,65}

$$r(mn:j_ij_f) = \frac{P(mn:j_ij_f)}{P(mn) \cdot n(j_i)},$$
(10)

and similarly, for elastic peaks

$$r(mn) = \frac{P(mn)}{P(00)},\tag{11}$$

where P(mn) is defined in Eq. (9). For the denominator of Eq. (10) it would have been more correct to use $P(mn:j_ij_i)$ but this probability cannot be extracted from the experimental results. The strong coupling between the rotational degrees of freedom and diffraction is expected to be more pronounced for the inelastic peaks and less important for the elastic $(j_i \rightarrow j_i)$ channel. Thus weighting P(mn) with the initial population of the rotational state j_i is an acceptable approximation. In theoretical calculations this quantity can be straightforwardly calculated by using Eq. (9).

Substituting Eq. (5) into Eqs. (10) and (11) leads to the expressions

$$r(mn:j_{i}j_{f}) = \frac{I(mn:j_{i}j_{f})}{I(mn)n(j_{i})} \sqrt{\frac{E_{i} + \Delta E_{rot}}{E_{i}}} \exp[2W_{mn:j_{i}j_{f}} - 2W_{mn}]$$
(12)

for the RID and

$$r(mn) = \frac{I(mn)}{I(00)} \exp[2W_{mn} - 2W_{00}]$$
(13)

for the elastic diffraction. An additional advantage of the evaluation in terms of these ratios is that the effects of the surface defects and the beam geometry cancel and any possible instability in the experiment and errors in the evaluation of the DW factors are significantly suppressed. Moreover, these ratios are well suited for comparison with theoretical calculations.

VI. THERMAL ATTENUATION OF THE PEAK INTENSITIES

As discussed in the previous section, the evaluation of transition probabilities from the scattering intensities at a fi-



FIG. 10. The surface temperature dependence of the intensities (peak area) of the peaks (00)(- \blacksquare -), (00:02)(- \bullet -), (-1-1) (- \blacktriangle -), and (-1-1:02) (- \blacktriangledown -) for D₂-LiF(001) along the $\langle 100 \rangle$ direction. E_i =85.3 meV (k_i =12.8 Å⁻¹). θ_{SD} =90°.

nite surface temperature requires the knowledge of the Debye temperature. To determine the Debye temperature, constant- θ_{SD} scattering experiments were carried out similar to the angular scans in Figs. 5 and 6 in both the $\langle 100 \rangle$ and $\langle 110 \rangle$ scattering directions as a function of surface temperatures between 130 and 600 K. Figure 10 displays a typical measured temperature dependence of the intensities of the specular, first order, and corresponding inelastic peaks. The deviations from the pure exponential expected in the Debye-Waller approximation are probably due to several effects. The Debye-Waller approximation, although it quite successfully accounts for x-ray and neutron scattering, is known to be only a crude approximation for the surface scattering of particles, especially at low collision energies for strongly interacting particles.⁶⁶

Tables III and IV list the best-fit slopes $2W(T_s)/T_s$ of all the major diffraction and RID peaks for each of the azimuths. Because of the marked deviations from the exponential behavior seen in Fig. 10 the slopes and Debye-Waller factors were evaluated over separate ranges of low and high temperatures. Using the data points between T_s = 130–310 K the measured intensities were extrapolated to 0 K. These intensities, denoted as I(0) in Tables III and IV, were used to calculate the absolute transition probabilities from Eq. (5). The corresponding values for P(mn) or $P(mn:j_i j_f)$ are listed in the final columns of these tables.

Surface Debye temperatures were calculated from Eqs. (6) and (7) using a well depth of D=35.3 meV, determined from selective surface adsorption experiments in the course of present investigations.⁴⁵ This value is consistent with the previously reported value of $D=37.7\pm4.4$ meV.⁶⁷ Debye temperatures calculated for each of the peaks and surfacet-emperature ranges are also listed in Tables III and IV. The average values of the Debye temperature Θ_D , excluding the

TABLE III. The surface temperature dependence of the D₂-LiF(001) peak intensities observed at incident angles θ_i for along the $\langle 100 \rangle$ direction with θ_{SD} =90°. The incident beam energy is E_i =85.3 meV and incident intensity is I_0 =28.4×10⁶ counts/s deg. The data is fitted to an exponential curve as in Eq. (6) to obtain the temperature independent attenuation parameter $-2W/T_s$ values for indicated temperature ranges. The corresponding Debye temperatures obtained using Eq. (6) are listed in the next column. From the measured intensities extrapolated to 0 K denoted by I(0) the absolute transition probabilities [$P = P(mn: j_i j_f)$] are listed in the final column.

θ_i [deg]	$(mn: j_i j_f)$	$-2W \times 10^3 / T_s \ (T_s \text{ range [K]})$	$\Theta_D [\mathrm{K}]^{\mathrm{a}}$	I(0)[counts/s deg]	$P \times 10^3$
13.94	(22:13)	15.6(130–190)	445†	12874	1.0
19.03	(22:02)	13.0(130–330)	490†	60964	3.2
24.83	(22)	12.5(130-310):14.5(330-450)	510:473†	260676	9.2
30.03	(11:02)	10.8(130-310):13.9(330-510)	540:476	433314	23.0
35.04	(11)	9.26(130-310):14.7(330-600)	600:476	461632	16.2
37.02	(00:13)	7.83(130-310):16.1(330-510)	653:455	82962	6.7
38.95	(11:20)	9.04(130-360)	626†	8044	4.0
40.70	(00:02)	8.65(130-310):13.0(330-600)	602:491	520290	26.6
45.00	(00)	7.90(130-310):12.7(330-600)	652:514	196474	6.9
48.29	(-1-1:13) ^b	8.65(130-310):11.2(330-510)	580:510	35082	2.8
51.38	(-1-1:02)	6.91(130-310):10.3(330-600)	666:546	71780	3.8
54.96	(-1-1)	7.21(130-310):12.7(330-600)	679:512	294562	10.4
57.66	(-1-1:20)	9.18(130-310)	627	11370	5.1
60.00	(-2-2:13)	6.46(130–310)	653†	5710	0.4
62.44	(-2-2:02)	7.95(130-310):13.5(330-480)	608:467	56570	2.8
65.19	(-2-2)	8.89(130-310):14.9(330-420)	604:466†	106774	3.7
74.84	(-3-3:02)	9.15(130-250)	552†	15262	1.5

^aThe values marked with a † have large errors due to the low intensity of the corresponding peaks. ^bThis peak overlaps with the (00:20) thereby the intensity includes also a small contribution from this peak.

θ_i [deg]	$(\mathbf{mn}: j_i j_f)$	$-2W \times 10^3 / T_s \ (T_s \text{ range [K]})$	$\Theta_D [\mathrm{K}]^\mathrm{a}$	I(0)[cps deg]	$P \times 10^3$
17.02	(30:02)	11.9(130-210)	512†	19145	1.0
23.50	(30)	13.6(130–330)	489†	67292	2.4
25.46	(20:02)	14.6(130–330)	464†	70284	3.7
29.28	(10:13)	13.8(130-270)	472†	85061	6.8
30.87	(20)	12.3(130-300):14.7(330-480)	518:474	341771	12.0
33.25	(10:02)	12.8(130-300):15.0(330-450)	498:459	216887	11.4
37.05	(00:13)	9.69(130-300):12.8(330-450)	558:485	237304	19.0
37.98	(10)	11.6(130-300):15.2(330-540)	537:469	826819	29.0
40.70	(00:02)	11.5(130-300):14.4(330-540)	523:467	715597	37.5
41.69	(10:20)	8.02(130-210)	667†	6239	2.8
45.00	(00)	9.51(130-300):13.1(330-540)	594:506	376451	13.3
48.23	(-10:02)	9.28(130-300):13.4(330-540)	577:480	289034	15.2
52.01	(-10)	10.5(130-300):14.7(330-540)	564:477	918901	32.1
53.02	(-20:13)	9.55(130-300):13.5(330-540)	547:459	140506	11.3
55.90	(-20:02)	11.1(130-300):14.7(330-540)	522:453	341218	17.9
59.13	(-20)	10.7(130-300):15.6(330-540)	555:460	361785	12.7
61.46	(-30:13)	9.38(130-300):13.4(330-450)	540:452	60588	4.9
63.74	(-30:02)	9.13(130-300):14.2(330-480)	566:454	99010	5.2
66.54	(-30)	9.30(130-300):13.5(330-390)	589:490†	68337	2.4

TABLE IV. The surface temperature dependence of the peak intensities for D₂-LiF(001) along the $\langle 110 \rangle$ direction with θ_{SD} =90°. See Table III for the details.

^aThe values marked with † have large errors due to the low intensity of the corresponding peaks.

values with large errors, indicated by a (†), are

$$\Theta_D = 577 \pm 50 \text{ K}$$
 for 130 K $\leq T_s \leq 310 \text{ K}$,

$$\Theta_D = 479 \pm 24 \text{ K}$$
 for 330 K $\leq T_s \leq 600 \text{ K}$. (14)

Here the error bars are the standard deviations based on the Θ_D values in Tables III and IV. Table V compares these results with the literature values of the Debye temperatures of the bulk LiF and for the (001) surface obtained with

TABLE V. Debye temperatures Θ_D of the LiF(001) surface. The values given in the parenthesis are the values without Armand correction. In the Armand correction the possibility of the interaction of the scattering particle with more than one surface atom is taken into account and the Debye temperatures are corrected according to the scattering geometry (Ref. 68).

$\Theta_D[\mathbf{K}]$	Reference	Remarks
734 K	85	Bulk value
335±33	86	He scattering
350±50 (513)	87	He scattering
415±44 (610)	88	H scattering
478 ± 10	45	He scattering
577 ± 50	This work	D_2 scattering ($T_s = 130 - 310$ K)
479±24	This work	D_2 scattering (T_s =330–600 K)

atomic scattering. The low temperature value Θ_D = 577±50 K is significantly larger than the previously measured values whereas the high temperature value of Θ_D = 479±24 K is reasonably consistent with the previous reports.

A careful analysis of the tabulated Debye temperatures in Tables III and IV reveals a slight difference between different azimuths as well as a small increase of Debye temperatures with increasing incident angle. These suggest the role of the scattering geometry in Debye-Waller attenuation.⁶⁸ For instance, with increasing incident angle, it is more likely that the scattering molecules interact with more surface atoms, leading to an increase in the average effective mass of the surface atoms in Eq. (6), thereby reducing the Debye-Waller attenuation. Since the dependences of the Debye temperature on the scattering axis and incident angle are small with respect to large error bars given in Eq. (14), they have been neglected in the present analysis.

It should be noted that with increasing surface temperature no significant broadening of peaks or shifting of the RID peak positions was observed. Moreover, the Debye temperatures obtained from the RID peaks are not systematically different from the values of elastic diffraction peaks. These observations indicate, in accordance with previous reports,¹⁵ that there is no significant role of the surface temperature in rotational excitation as in molecular scattering from metal surfaces.^{69,70} The present results for D₂-LiF(001) indicate that the elastic diffraction and the RID processes can be modeled using a static lattice and neglecting phonon inelastic transitions.



<100>

FIG. 11. The diffraction and RID peak-area intensities for D_2 -LiF(001) along the $\langle 100 \rangle$ direction (a) and along the $\langle 110 \rangle$ direction (b) for constant incident angles of 30° , 45° , and 60° . $I_0 = 28.4 \times 10^6$ counts/s deg. The specular peaks are indicated by heavy vertical lines.

VII. RESULTS AND DISCUSSION

In this section the measured peak-area intensities for the elastic diffraction and RID peaks are presented as functions of incident and final angles and analyzed in terms of probability ratios. Figure 11 shows some typical peak-area intensities as a function of the final angle for three different incident scattering angles for both symmetry directions. Although the number of kinematically allowed channels is higher for the lower angles of incidence, the number of observed peaks at $\theta_i = 30^\circ$ is low, since the lowest total angle in the present experiments was $\theta_{SD} = 56^{\circ}$ so that peaks with minus indices and low incident angles were outside the measured range. Several trends can be seen from the data. For $\theta_i = 60^\circ$, which comes closest to grazing incidence, the specular peak is larger than both the diffraction and the RID peaks. The inelastic intensities are smaller by about an order of magnitude. At more normal incidence at $\theta_i = 30^\circ$ the specular peak no longer dominates and the inelastic RID peaks are much larger and comparable to the elastic diffraction peaks. Also the absolute intensities decrease by about an order of magnitude. Some of the decrease can be attributed to the larger DW attenuation resulting from the increase in k'_{iz} and k'_{fz} which enter into the kinematical factor of Eq. (6).

More information is obtained by plotting the different peak-area intensities as a function of the incident angle. The final angles for each diffraction process are defined by the kinematical equations given in Eqs. (2) and (3). Figure 12 shows an overview of the peak area intensities of the elastic diffraction peaks and the corresponding intensity ratios with respect to the specular peak. All the peak intensities first increase in intensity with increasing incident angle. This effect, seen already in Fig. 11, can be attributed to a number of factors, of which the DW attenuation is expected to be the most important. Then at some critical angle the (22) and (11)diffraction peaks in the (100) azimuth and the (20) and (10) diffraction peaks in the $\langle 110 \rangle$ azimuth fall off abruptly as they approach the critical angles for which the diffraction is no longer kinematically allowed. The critical angles are indicated by vertical dashed and dotted lines. The fall-off of the specular peaks along both azimuths and the elastic (-1)-1), (-2-2), (-10), and (-20) diffraction peaks beyond about 70° results from the reduced effective area of the incident beam which strikes the crystal surface, which is described by the factor $\eta(\theta_i)$ in Eq. (5), but cancels in the ratios of Eqs. (10)–(13).

In the $\langle 110 \rangle$ direction the peak intensities exhibit a remarkable sharp dip at the incident angle of about 78°. Not only the intensity of these elastic peaks, but also, as can be



FIG. 12. The peak-area intensities of specular and elastic diffraction peaks (a) for the $\langle 100 \rangle$ and (b) for the $\langle 110 \rangle$ azimuthal directions. The corresponding ratios of the peak-area intensities to the specular peak are shown in (c) and (d), respectively. Vertical dashed and dotted lines denote the critical angles for the first- and second-order diffraction peaks, respectively. $P_0=120$ bar, $T_0=300$ K, and $E_i=85.3$ meV.

seen in Fig. 9, the RID peaks and the inelastic background intensity are severely suppressed at this angle. The reason for this anomaly is at present still not completely understood. It could be due to an interference effect between the surface steps which is clearly observed for well-defined stepped surfaces.^{71,72} On the other hand, such interference effects should depend also on the final beam energy and should therefore be different for the RID peaks. Since it is well-localized to a narrow range of incident angles, the sharp dip was neglected in determining the peak ratios and thus has no effect on the analysis.

The peak ratios, determined using the peak-area intensities and Eq. (13), are plotted in Figs. 12(c) and 12(d). These reveal a sharp peak for the (11) and (10) diffraction peaks with large relative intensities of about 3. The corresponding negative order diffraction peaks have much smaller intensities which after rising to a maximum decrease nearly monotonously with increasing incident angle. The other diffraction peak ratios in both surface azimuths also tend to decrease with increasing incident angle. Qualitatively this can be explained as follows: With increasing incident angle the perpendicular component of the incident energy decreases, so that their penetration into the repulsive region of the potential decreases. The effective corrugation felt by the incident particle is thus reduced. Although the maxima in the r(11) and r(10) are suggestive of surface rainbows,^{24,25,73–75} comparison with the intensities in Figs. 12(a) and 12(b) suggest, however, that the maxima are more likely simply caused by the sudden kinematical cutoff of the diffraction. The factors determining the initial rise in the ratios at small incident angles are not fully understood.

Figure 13 shows the evolution of peak-area intensities of the specular peaks and the associated rotational transitions $(0 \rightarrow 2)$ and $(1 \rightarrow 3)$ and, in separate plots, their ratios to the specular peak as a function of incident angle. In a quite similar way as the diffraction peaks both the specular and the rotationally inelastic peak-area intensities increase with increasing incident angle. This trend correlates nicely with the decreasing number of channels and decreasing DW factors. With further increasing incident angle along the $\langle 100 \rangle$ azimuth the intensity of the $(0 \rightarrow 2)$ transition peak then decreases dramatically as it approaches the kinematically forbidden angle and finally disappears. Unfortunately, the (00:13) peak in the $\langle 100 \rangle$ azimuth overlaps with another peak



FIG. 13. The peak-area intensities of specular and RID peaks (a) for the $\langle 100 \rangle$ and (b) for the $\langle 110 \rangle$ azimuthal directions. The corresponding ratios of the peak-area intensities to the specular peak are shown in (c) and (d), respectively. Vertical dashed and dotted lines denote the critical angles for the $(0 \rightarrow 2)$ and $(1 \rightarrow 3)$ rotational transition peaks, respectively. $P_0=120$ bar, $T_0=300$ K, and $E_i=85.3$ meV.

for higher incident angles than 40°, so that its intensity cannot be extracted up to the critical angle. Surprisingly, the *r*-values, plotted in parts (c) and (d) of Fig. 13, for the $\langle 100 \rangle$ azimuth are almost insensitive to the incident angle up to the kinematically forbidden zone. This, however, is not a general rule, but rather an exception as is apparent from a comparison with the rotational transitions along the $\langle 110 \rangle$ azimuth. There the ratios for both the $(0 \rightarrow 2)$ and the $(1 \rightarrow 3)$ transitions axis show a strong dependence on the incident angle. They rise to maxima at about $\theta_i = 37^\circ$ and then decrease steeply as they approach the corresponding kinematically critical angles.

A very remarkable feature of the RID ratios for both the $(0 \rightarrow 2)$ and the $(1 \rightarrow 3)$ transitions is that the rotational transition probabilities are greater than one. Such extremely large transition probabilities are also observed in D₂ scattering from NaF.¹⁵ For D₂ scattering from metal surfaces, on the other hand, the RID ratios remain less than 30% even for incident energies up to 250 eV,^{76,77} which is consistent with the smaller corrugation of the metal surfaces.

In Fig. 14 the intensities of the same rotational transitions associated with the (-1-1) and the (-10) diffraction peaks

and their ratios with respect to the corresponding diffraction peaks are presented for both symmetry axes. The peak-area intensities in parts (a) and (b) show a similar increase with increasing incident angles as found for the specular peak inelastic transition (Fig. 13), but the signals are overall somewhat smaller. The ratios are, however, with the exception of (-10:02), all less than unity. This is a clear indication for a strong coupling between diffraction and rotational inelasticity. If these processes were decoupled then the ratios in Figs. 13(c), 13(d), 14(c), and 14(d) should all be about the same. To be sure a direct comparison is not completely justified since the range of allowed angles is greatly restricted for the specular peak compared to the first order diffraction peaks.

This result is in contradiction with the decoupling of diffraction and rotational transitions which has been discussed extensively and found to be quite well satisfied in several approximate model calculations.^{28,30–32} For example, on the basis of their close-coupling calculations²⁸ Drolshagen *et al.* concluded from model calculations for H₂-LiF(001) that at higher incident energies of 0.5–0.7 eV, diffraction and rotational transitions are decoupled provided that both the corru-



FIG. 14. The peak-area intensities of first order diffraction peaks and their related rotational inelastic peaks (a) for the $\langle 100 \rangle$ and (b) for the $\langle 110 \rangle$ azimuthal directions. The corresponding ratios of the peak-area intensities to the (-1-1) and (-10) diffraction peaks are shown in (c) and (d), respectively. Vertical dashed lines denote the critical angles for the $(1 \rightarrow 3)$ rotational transition peaks. $P_0=120$ bar, $T_0=300$ K, and $E_i=85.3$ meV.

gation and the anisotropy are not too large. This suggests that the observed strong coupling in D_2 -LiF(001) is probably due to the lower collision energies and the greater time for interacting with the surface. Moreover, for the smaller values of incident energies simple energetical threshold effects dominate over dynamical considerations. For instance, as the incident energy approaches the rotational transition energy the transfer of the normal component of the incident beam energy to the parallel component competes with the rotational transition.

The dramatic increase in the (-10:02) ratio at the large incident angles beyond $\theta_i = 70^\circ$ corresponding to grazing collisions is especially noteworthy. As seen from the intensities in Fig. 14(b) this is due to a less sharp decrease in the peak area intensity of the rotationally inelastic peak compared to the elastic diffraction peak. A likely explanation is a resonance between the rotations of the molecule and the frequency felt by the molecule as it moves nearly parallel to the surface. In a classical approximation⁷⁸ the rotational frequency of a molecule is given by

$$\nu_{rot}(j) = 2Bcj, \tag{15}$$

where *B* is the rotational energy constant $[B(D_2) = 30.4 \text{ cm}^{-1}]$, *c* is the speed of light, and *j* is the rotational state. Thus for a rotational transition $j=0 \rightarrow 2$ the rotational period is given by

$$\tau_{rot} = 8B = 1.4 \times 10^{-13} \text{ s},\tag{16}$$

where an additional factor of 2 is included to account for the two equal ends of the D_2 molecule. As a result of the protruding F-atoms, the molecules with an incident angle of 82° along the $\langle 110 \rangle$ direction experience an oscillatory perturbation with a period, given by,

$$\tau_{mol} = \frac{d}{v_i \sin(\theta_i)} = 1.4 \times 10^{-13} \text{ s}, \tag{17}$$

where d=2.84 Å and $v_i=2.0310^3$ m/s ($k_i=12.8$ Å⁻¹). Thus,

since both periods are the same, the rotations couple resonantly to the translational motion resulting in an extremely strong diffraction-rotational coupling.

VIII. SUMMARY

A new atom/molecule surface scattering apparatus is described which permits a wide range of final scattering angles to be scanned for any incident angle in the full range from 0° to 90° decoupled from the final angle. By incorporating several differential pumping stages in the incident beam and scattered beam lines the detector background has been significantly reduced so that angular distributions with a high resolution of $\delta\theta$ =0.2° are possible. High resolution time-offlight spectra can also be measured. The potential of this new machine is demonstrated in a comprehensive study of the elastic and rotationally inelastic diffraction peaks in the scattering of D₂-molecules from the single crystal LiF surface. As a result of the wide range of accessible final angles over 21 peaks could be observed or identified in the $\langle 100 \rangle$ direction and more than 28 peaks could be identified in the $\langle 110 \rangle$ direction.

The results for both azimuths have been analyzed for the first- and second-order elastic diffraction peak-area intensities relative to the specular peaks. From the peak-area intensities diffraction probabilities are obtained by normalizing with the incident beam intensity, which is measured directly by positioning the detector in the forward direction. Additional

corrections account for the Debye-Waller attenuation, the effect of the change in velocities (in the case of rotational transitions) on the detector sensitivity, the fractional population of the initial rotational state, and geometric factors. The elastic diffraction probabilities rise to a maximum of about 300% with increasing incident angles and then fall off sharply as the kinematically limiting angles are approached. The large diffraction probabilities appear to be related to the very steep hard repulsion of the He-LiF(001) potential combined with the relatively large corrugation amplitude of 0.3 Å.^{24,79}

The probabilities for the rotational transitions $j=0\rightarrow 2$ and $1 \rightarrow 3$ relative to the specular peak exhibit a somewhat similar behavior and equally large transition probabilities. Thus elastic diffraction and rotational transitions have nearly the same probabilities. Much smaller transition probabilities of less than about 50% are found for rotational transitions associated with a first-order diffraction peak. The results thus indicate that the diffraction process inhibits the rotational transitions in the accessible cases in which diffraction leads to an increase in the final angle compared to the incident angle. An exception is observed at grazing incidence θ_i \geq 70° along the (110) direction for which the rotational transition $i=0 \rightarrow 2$ is still allowed and increases up to a 300% probability at the largest accessed angle of 82°. This dramatic enhancement is explained by a classical resonance in which the perturbation produced by the molecule moving nearly parallel to the regular array of protruding F-atoms of the surface has the same period as the classical rotations of the molecules when excited into the j=2 state.

In addition the Debye-Waller attenuations of 17 peaks in the $\langle 100 \rangle$ direction and 19 peaks in the $\langle 110 \rangle$ direction have been measured for surface temperatures between 130 and 600 K. A nonexponential behavior is found for many of the peaks with significantly larger Debye temperatures at the lower temperatures (130-310 K) compared to temperatures greater than 330 K. Individual peaks also show significant differences in the Debye temperatures, but clear trends could not be established. The observed relatively poor agreement of the thermal attenuation with the Debye-Waller model, in comparison to He-LiF(001) and molecular scattering from metal surfaces,^{76,77} can be related to the effects which are not properly accounted for in the simple impulsive model used to evaluate the Debye-Waller attenuation. Overall, however, the results appear to be in reasonable agreement with the conclusions of Brusdeylins et al.¹⁵ and differ from the systems such as molecular scattering from metal surfaces^{69,70} and I₂ scattering from MgO(001).⁸⁰ In summary, it appears that for D₂-LiF(001) at thermal collision energies a rigid-surface treatment in theoretical analysis can successfully account for the rotational transition probabilities.

The scattering of $H_2(D_2)$ molecules from LiF(001) is certainly the simplest of all molecule surface scattering systems, especially when it is realized that the ionic LiF surface is free of extensive relaxation⁸¹ and rumpling⁸² and compared to most other surfaces is very inert. Also it is the first moleculesurface scattering system studied already in 1930⁶ and extensively studied since then. Yet, the present new extensive experimental data go far beyond previous experiments and provide new challenges for a theoretical understanding. As discussed in the Introduction open questions revolve about the roles of the electrostatic molecular quadrupole surfaceion interactions and their effect on the orientation *m*-dependence of the molecular rotation on the scattering probabilities. Hopefully, a full close coupling calculation¹⁸ for a realistic potential which includes the major attractive dispersion, electrostatic, and induction terms and comparisons with these new experimental results will provide the answers to some of these questions.83

In the future it will be interesting to explore the coupling to surface phonons and further clarify the role of Δm transitions on the diffraction, rotational inelastic, and phonon inelastic processes. A first step in this direction was recently achieved in a related study of H₂-scattering from NaF, where an unexpected coupling of Δm transition to shear horizontal phonons was observed.³⁴

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- ¹J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. 4, 1 (1985).
- ²R. B. Gerber, Chem. Rev. (Washington, D.C.) **87**, 29 (1987).
- ³A. Capellini and A. P. J. Jansen, J. Chem. Phys. **104**, 3366 (1996).
- ⁴M. Ehara, H. D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **105**, 8865 (1996).
- ⁵A. C. Luntz, J. K. Brown, and M. D. Williams, J. Chem. Phys. **93**, 5240 (1990).
- ⁶I. Estermann and O. Stern, Z. Phys. **61**, 95 (1930).
- ⁷R. Frisch and O. Stern, Z. Phys. **84**, 430 (1933).
- ⁸D. R. O'Keefe, J. N. Smith, R. L. Palmer, and H. Saltsburg, Surf. Sci. **20**, 27 (1970).
- ⁹D. R. O'Keefe, J. N. Smith, R. L. Palmer, and H. Saltsburg, J. Chem. Phys. **52**, 4447 (1970).
- ¹⁰R. G. Rowe and G. Ehrlich, J. Chem. Phys. **63**, 4648 (1975).
- ¹¹R. G. Rowe, L. Rathbun, and G. Ehrlich, Phys. Rev. Lett. 35, 1104 (1975).
- ¹²G. Boato, P. Cantini, and L. Mattera, J. Chem. Phys. 65, 544 (1976).
- ¹³E. Kolodney and A. Amirav, Surf. Sci. **155**, 715 (1985).
- ¹⁴W. Allison and B. Feuerbacher, Phys. Rev. Lett. **45**, 2040 (1980).
- ¹⁵G. Brusdeylins and J. P. Toennies, Surf. Sci. **126**, 647 (1983).
- ¹⁶G. Brusdeylins, G. Drolshagen, A. Kaufhold, J. Skofronick, and J. P. Toennies, Surf. Sci. **189/190**, 972 (1987).
- ¹⁷M. F. Bertino, A. L. Glebov, J. P. Toennies, F. Traeger, E. Pijper, G.-J. Kroes, and R. C. Mowrey, Phys. Rev. Lett. **81**, 5608 (1998).
- ¹⁸G.-J. Kroes and R. C. Mowrey, J. Chem. Phys. **103**, 2186 (1995).
- ¹⁹E. Pijper and G.-J. Kroes, Phys. Rev. Lett. **80**, 488 (1998).
- ²⁰R. M. Logan, Mol. Phys. **17**, 147 (1969).
- ²¹J. Halbritter, Z. Naturforsch. A **29a**, 1723 (1974).
- ²²N. Cabrera, V. Celli, F. O. Goodman, and R. Manson, Surf. Sci. 19, 67 (1970).
- ²³F. O. Goodman and W. S. Liu, Surf. Sci. 49, 417 (1975).
- ²⁴U. Garibaldi, A. C. Levi, R. Spadacini, and G. E. Tommei, Surf. Sci. **48**, 649 (1975).
- ²⁵U. Garibaldi, A. C. Levi, R. Spadacini, and G. E. Tommei, Surf. Sci. **55**, 40 (1976).
- ²⁶G. Wolken, J. Chem. Phys. **59**, 1159 (1973).
- ²⁷G. Wolken, Jr., J. Chem. Phys. **62**, 2730 (1975).
- ²⁸G. Drolshagen, A. Kaufhold, and J. P. Toennies, J. Chem. Phys. 83, 827 (1985).
- ²⁹R. B. Gerber, A. T. Yinnon, Y. Shimoni, and D. J. Kouri, J. Chem. Phys. **73**, 4397 (1980).
- ³⁰R. B. Gerber, L. H. Beard, and D. J. Kouri, J. Chem. Phys. 74, 4709 (1981).
- ³¹L. M. Hubbard and W. H. Miller, J. Chem. Phys. 78, 1801 (1983).
- ³²S. Saini, D. A. Dows, and H. S. Taylor, Chem. Phys. **90**, 87 (1984).
- ³³N. R. Hill, Phys. Rev. B **19**, 4269 (1979).
- ³⁴G. Benedek, F. Traeger, and J. P. Toennies, Phys. Rev. Lett. **94**, 086103 (2005).
- ³⁵R. B. Doak, Ph.D. thesis, Massachusetts Institute of Technology, Boston, 1981.
- ³⁶R. Vollmer, Ph.D. thesis, Georg-August Universität, Göttingen, Germany, 1992.

- ³⁷R. David, K. Kern, P. Zeppenfeld, and G. Comsa, Rev. Sci. Instrum. **57**, 2771 (1986).
- ³⁸T. Miyake, E. S. Gillman, I. Oodake, and H. Petek, Jpn. J. Appl. Phys., Part 1 **36**, 4531 (1997).
- ³⁹G. Brusdeylins, R. B. Doak, and J. P. Toennies, Phys. Rev. B 27, 3662 (1983).
- ⁴⁰J. M. Horne and D. R. Miller, J. Vac. Sci. Technol. **13**, 351 (1976).
- ⁴¹G. Boato, P. Cantini, and L. Mattera, Surf. Sci. 55, 141 (1976).
- ⁴²T. Engel and K. H. Rieder, Surf. Sci. **109**, 140 (1981).
- ⁴³G. Lilienkamp and J. P. Toennies, J. Chem. Phys. 78, 5210 (1983).
- ⁴⁴R. B. Doak, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, New York, 1992), Vol. 2, p. 384.
- ⁴⁵Y. Ekinci, Ph.D. thesis, Georg-August Universität, Göttingen, Germany, 2003, http://webdoc.sub.gwdg.de/diss/2004/ekinci/ index.html.
- ⁴⁶Model DeTech-418, Detector Technology Inc., Palmer, MA.
- ⁴⁷SERA-5142: Seybert&Rahier GmbH Co., Immenhausen, Germany.
- ⁴⁸Grade 2.8: Linde AG, 85716 Unterschleissheim, Germany.
- ⁴⁹ M. Faubel, F. A. Gianturco, F. Ragnetti, L. Y. Rusin, F. Sondermann, and U. Tappe, J. Chem. Phys. **101**, 8800 (1994).
- ⁵⁰Karl Korth Kristalle GmbH, Altenholz, Germany.
- ⁵¹S. J. Burns and W. W. Webb, J. Appl. Phys. **41**, 2086 (1970).
- ⁵²M. J. Yacaman and T. Ocana, J. Appl. Phys. 48, 418 (1977).
- ⁵³H. Höche and H. Bethge, J. Cryst. Growth **33**, 246 (1976).
- ⁵⁴R. V. D. Schmicker, J. P. Toennies, and H. Weiss, J. Chem. Phys. 95, 9412 (1991).
- ⁵⁵G. Lange, J. P. Toennies, R. Vollmer, and H. Weiss, J. Chem. Phys. **98**, 10096 (1993).
- ⁵⁶J. Estel, H. Hoinkes, H. Kaarman, H. Nahr, and H. Wilsch, Surf. Sci. 54, 393 (1976).
- ⁵⁷J. W. Mathews and E. Gruenbaum, Philos. Mag. **11**, 1233 (1965).
- ⁵⁸P. Barraclough and P. G. Hall, Surf. Sci. **46**, 393 (1974).
- ⁵⁹G. Benedek, G. Brusdeylins, R. B. Doak, J. G. Skofronick, and J. P. Toennies, Phys. Rev. B 28, 2104 (1983).
- ⁶⁰H. Legge, J. R. Manson, and J. P. Toennies, J. Chem. Phys. **110**, 8767 (1999).
- ⁶¹F. Traeger, Ph.D. thesis, Georg-August Universität, Göttingen, Germany, 2001.
- ⁶²A. C. Levi and H. Suhl, Surf. Sci. 88, 227 (1979).
- ⁶³F. Hofmann, J. R. Manson, and J. P. Toennies, J. Chem. Phys. 101, 10115 (1994).
- ⁶⁴J. L. Beeby, J. Phys. C 4, L359 (1971).
- ⁶⁵ M. F. Bertino, F. Hofmann, and J. P. Toennies, J. Chem. Phys. 106, 4327 (1997).
- ⁶⁶H. D. Meyer, Surf. Sci. 104, 117 (1981).
- ⁶⁷R. J. LeRoy, Surf. Sci. **59**, 541 (1976).
- ⁶⁸G. Armand, L. Lapujoulade, and Y. Lejay, Surf. Sci. **63**, 143 (1977).
- ⁶⁹G. Darling, Gas-Surf. News **34**, 2 (2002).
- ⁷⁰H. F. Busnengo, W. Dong, P. Sautet, and A. Salin, Phys. Rev. Lett. 87, 127601 (2001).
- ⁷¹S. Terreni, P. Cantini, M. Canepa, and L. Mattera, Phys. Rev. B 56, 6490 (1997).
- ⁷²B. Croset and C. de Beauvais, Surf. Sci. **409**, 403 (1998).
- ⁷³J. D. McClure, J. Chem. Phys. **52**, 2712 (1970).
- ⁷⁴G. Boato, P. Cantini, U. Garibaldi, A. C. Levi, L. Mattera, R.

Spadacini, and G. E. Tommei, J. Phys. C 6, L394 (1973).

- ⁷⁵F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic Press, New York, 1976).
- ⁷⁶M. F. Bertino and D. Farias, J. Phys.: Condens. Matter 14, 6037 (2002).
- ⁷⁷D. Farias, R. Miranda, and K. H. Rieder, J. Chem. Phys. **117**, 2255 (2002).
- ⁷⁸G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 1: *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
- ⁷⁹N. Garcia, V. Celli, and F. O. Goodman, Phys. Rev. B **19**, 634 (1979).
- ⁸⁰R. Elber and R. B. Gerber, Chem. Phys. Lett. **119**, 269 (1985).

- ⁸¹Y. Ekinci and J. P. Toennies, Surf. Sci. 563, 127 (2004).
- ⁸²J. Vogt and H. Weiss, Surf. Sci. 501, 203 (2002).
- ⁸³R. Valero, G.-J. Kroes, Y. Ekinci, and J. P. Toennies (unpublished).
- ⁸⁴K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 4 (Van Nostrand, New York, 1978).
- ⁸⁵J. T. Lewis, A. Lehoczky, and C. V. Briscoe, Phys. Rev. 161, 877 (1967).
- ⁸⁶G. Vidali and C. Hutchings, Phys. Rev. B **37**, 10374 (1988).
- ⁸⁷J. R. Bledsoe and S. S. Fisher, Surf. Sci. **46**, 129 (1974).
- ⁸⁸H. Hoinkes, H. Nahr, and H. Wilsch, Surf. Sci. 33, 516 (1972);
 40, 457(E) (1973).