

## Otto Stern and the double bank shot

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In analogy to a double surface scattering study of Estermann, Frisch and Stern for selecting and detecting the velocity of a beam of particles, it is proposed to use double surface scattering to investigate the collision dynamics of a beam of polarized particles with a known surface. In this proposed experiment, the first surface scattering event prepares a polarized (aligned/oriented) beam of particles, and the second surface scattering event permits the measurement of how the polarized beam interacts with the surface under study.

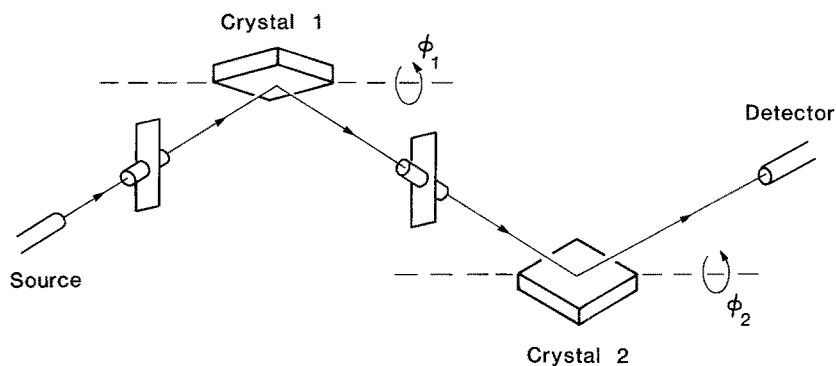
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The genius of Otto Stern is apparent in a number of pioneering experiments designed to test theory, particularly through the use of molecular beam techniques. Indeed, Stern authored and coauthored thirty papers with the subtitle “Untersuchungen zur Molekularstrahlmethode” which appeared in the *Zeitschrift für Physik* between 1926 and 1933 [1]. However, Stern’s use of the molecular beam method to test theory antedates 1926. For example, Stern is probably best remembered for the celebrated Stern-Gerlach experiment [2, 3] (1921) which was the first direct measurement of a magnetic moment of an atom and which established the reality of space quantization of angular momentum in a magnetic field at a time when the predictions of the new quantum theory were keenly felt to be in conflict with classical concepts. Stern also carried out experiments on the direct determination of the thermal velocity distributions of atoms and molecules in beams [4, 6]. In earlier work he and Volmer developed the standard method of extracting kinetic rate constants from bulb experiments as a function of pressure by using “the collision clock” to time quenching rates (Stern-Volmer kinetics [7]).

Much less known are Stern’s contributions to surface science. As part of Stern’s ambitious molecular beam program [5], he sought to demonstrate the real-

ity of the Broglie waves associated with material particles and to test quantitatively the relation  $\lambda = h/mv$ , where  $\lambda$  is the de Broglie wavelength,  $h$  is Planck’s constant,  $m$  is the mass of the particle and  $v$  is its velocity. In 1930 Estermann and Stern [8] investigated the scattering of He and H<sub>2</sub> from single-crystal surfaces of NaCl and LiF. They found that the intensity of the scattered beam recorded as a function of angle showed clearly discernible diffraction maxima. They also developed in great detail the theory of diffraction for beams scattering for periodic lattices, which serve as a diffraction grating for the “matter waves.” This work not only allowed a direct verification of the de Broglie relationship but also permitted the determination of the effective grating constant of the crystal lattice.

The next year (1931) witnessed an important refinement of this experiment by Estermann, Frisch and Stern [9]. They narrowed the He atom velocity distribution using a velocity selector consisting of a concentric pair of rotating chopper wheels. In this way, Estermann et al. were able to confirm the de Broglie relation to an accuracy of 1%. Today, He atom diffraction studies are one of the most sensitive means to examine surface structure [10], to learn about surface motions [11–14] (phonon-spectra), and even to study phase transitions of surface adlayers [15].



**Fig. 1.** Schematic diagram, adapted from Fig. 1 of Ref. 9, showing a double surface scattering event. The two collimators are fixed, while the two crystal surfaces are free to be tilted

However, the paper by Estermann, Frisch and Stern [9] has another feature which has fascinated me. They report what appears to be the first double surface scattering experiment – what I shall call in the parlance of Americal pool “the double bank shot.” In this experiment a beam of He atoms is first scattered off one LiF crystal surface; a diffracted beam, selected in direction, is allowed to impinge on a second LiF crystal surface; and the intensity of the resulting diffracted beam from the second scattering event is then recorded. The concept is very appealing. The first surface scattering event prepares a velocity-selected beam of He atoms from the incoming Maxwellian distribution of incident beam particles; the second surface scattering event analyzes the prepared distribution as to how monochromatic (monoenergetic) it is [16].

Clearly this is an experimental tour de force when it is recognized that this study was carried out more than fifty years ago, long before ultra high vacuum conditions (pressures less than  $10^{-9}$  Torr) could be routinely achieved, let alone measured! An examination of this experiment is quite instructive.

Figure 1 pictures the schematic setup. Rather than deal with the complications of having movable slits inside a vacuum chamber, Estermann, Frisch and Stern [9] employ two fixed slits but vary the orientation of both crystal surfaces by mounting them on heated tilt tables. Each tilt table is attached to a slotted knitting needle, and a screwdriver, external to the vacuum chamber, permits the tilt angle of the table to be set. The incident He beam strikes the surface of the first LiF crystal along a principal axis of the crystal, in particular, along alternating rows of  $\text{Li}^+$  and  $\text{F}^-$  ions. The fixed slit is set to accept beam scattered at the specular angle. The LiF crystal is tilted (rotated) about the alternating rows of  $\text{Li}^+$  and  $\text{F}^-$ , and this tilt angle is denoted by  $\phi$ . The second LiF crystal is oriented in the same manner as the first and it is also capable of being tilted in the same way.

Figure 2 presents top and side views of the beam apparatus. One reason for the success of this experiment is the choice of the highly corrugated LiF crystal surface, which remains atomically clean in poor vacuum. Estermann, Frisch and Stern estimated the absolute pressure to be only about  $10^{-5}$  Torr, but in retrospect [17], it was likely much lower ( $10^{-7}$ – $10^{-8}$  Torr). Another reason for the success of this experiment is the ingenious detection scheme. The scattered He beam impinges on an orifice in a small tube connected to a manometer. The pressure builds up in the receiving tube until the number of He atoms entering the tube is counterbalanced by the number of He atoms escaping the tube. The manometer forms part of a Wheatstone bridge circuit which drives a galvanometer. In this manner pressure changes as small as  $10^{-9}$  Torr could be detected. Figure 3 displays the He atom diffraction data obtained from scattering off the second LiF crystal when the orientation of the first LiF crystal is held fixed at different values of  $\phi_1$ . The intensities of the diffraction maxima follow closely the behavior expected from an incoming Maxwellian beam of He atoms.

Subsequent studies by Frisch and Stern [18] in 1933 led to the discovery of bound state resonance scattering, also called selective adsorption. Using the same type of experimental setup, Frisch and Stern showed that under certain conditions the He atoms impinging on the LiF crystal may be diffracted in such a manner so as to be captured by the surface field [19, 20], causing pronounced minima to appear in the intensity of the diffracted beam.

The idea of double surface scattering sparks my imagination. It suggests to me the possibility of investigating how aligned or oriented molecules interact with a surface [21]. In experimental studies of most collisional phenomena we must accept a large number of averages – averages over impact parameter, over collision geometry orientation, over initial relative velocity, and over final state translational and internal

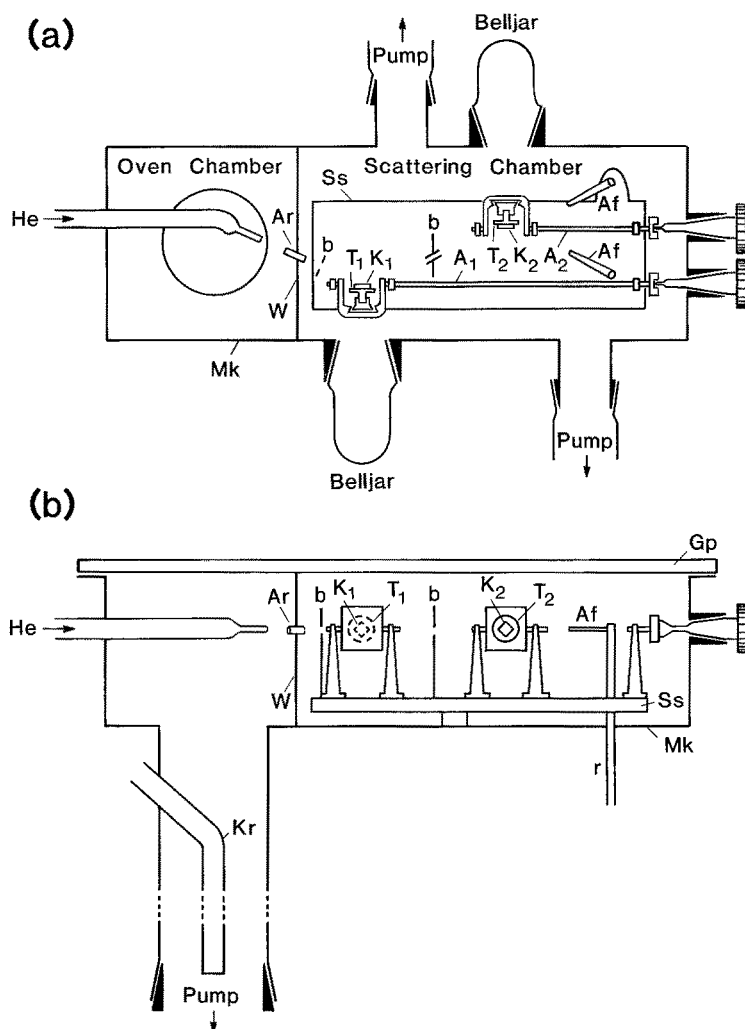


Fig. 2a and b. Beam apparatus, adapted from Fig. 2 of Ref. 9, showing (a) top view, and (b) side view.

Symbols have the following meanings: *Mk* = brass; *W* = wall; *Ss* = steel support assembly; *Ar* = skimmer; *b* = collimator; *T* = tilt table; *K* = crystal; *Af* = orifice entrance to manometer; *A* = knitting needle actuator; *Gp* = glass plate; *r* = small tube leading to manometer; and *Kr* = cold trap filled with liquified air

energy distributions. These averages hide individual collision events and hence confound our understanding of the forces operative during the collision event. The ability to collide polarized beams of particles with chosen surfaces helps to undo one of these averages; this may reveal much more information about the detailed nature of the collision process.

Double surface scattering is routine in neutron spectroscopy where a crystal lattice serves as a grating spectrometer to produce a monochromatic incident beam and another grating spectrometer serves to analyze the energy distribution of the scattered neutrons. However, there appear to be almost no examples to date of experiments in which polarized beams of atoms or molecules were purposely scattered from well-defined surfaces. An exception is the work of Muessig and Diebold [22] who have studied the collisions of optically aligned sodium atoms with heated LiF surfaces in a vacuum chamber at typically  $10^{-6}$  Torr. Scattering experiments utilizing polarized

molecular beams have primarily relied on the use of inhomogeneous electric fields (via a hexapole rod configuration) to orient polar, symmetric-top molecules [23–25]. Other techniques are also possible, such as optical pumping in the infrared [26, 27] or optical absorption, saturation or photodissociation in the visible and ultraviolet [22, 28–31].

The scattering of a beam of molecules from a surface may also be used to prepare a directed beam of polarized molecules [32–35]. This method takes advantage of the anisotropic forces which during the collision act mostly along the local surface normal to prepare a polarized distribution of molecules. For example, if the molecule-surface scattering event is approximated as an encounter of a hard ellipsoid with a flat surface, then it is readily seen (Fig. 4) that the angular momentum vector  $\mathbf{J}$  of the molecule lies preferentially in a plane parallel to the surface, and the resulting beam of scattered molecules is strongly aligned [36] with its plane of rotation perpendicular

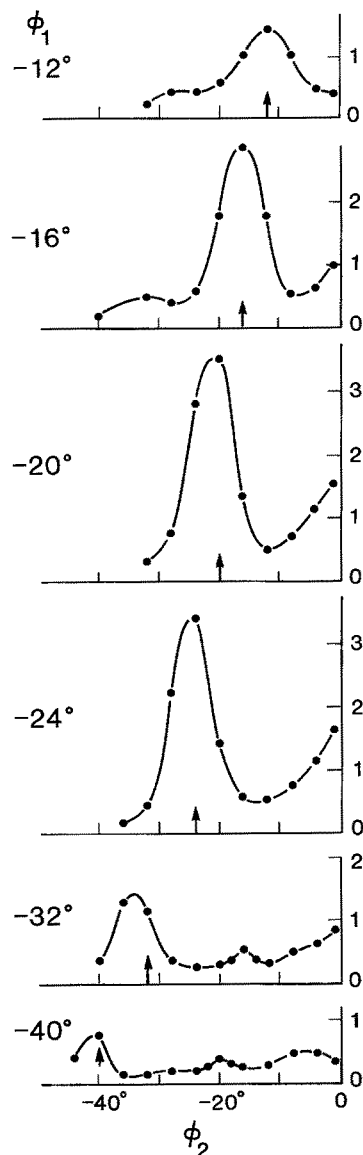


Fig. 3. He atom scattering signal as a function of the second crystal tilt angle  $\phi_2$  for different values of the first crystal tilt angle  $\phi_1$ . The arrow in each event locates the diffraction maximum. This figure is adapted from Fig. 8 of Ref. 9

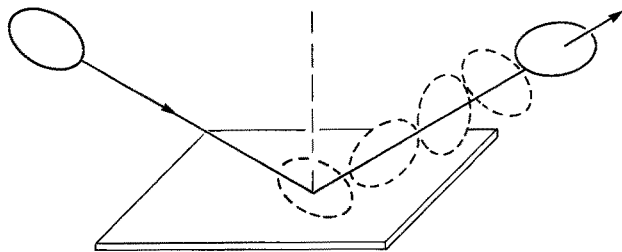


Fig. 4. Diatomic molecule-flat surface scattering producing a beam of aligned molecules. The diatomic molecules are treated as hard, nearly spherical ellipsoids, which is a good approximation for a homonuclear molecule, like  $N_2$

to the surface. This method for preparing a polarized beam of molecules appears to be quite general. It neither requires the molecules to be polar nor to absorb radiation in some convenient portion of the electromagnetic spectrum. In addition, the molecule-surface scattering method has the advantages that the flux is substantial and the degree of alignment/orientation can be sizeable.

A simple measure of the alignment is the quadrupole moment of the  $\mathbf{J}$  distribution,  $A_{0+}^{(2)}(J)$ , defined by

$$A_{0+}^{(2)}(J) = \langle (3J_z^2 - \mathbf{J}^2)/\mathbf{J}^2 \rangle \\ = 2\langle P_2(\cos \theta) \rangle, \quad (1)$$

where the brackets  $\langle \dots \rangle$  denote an ensemble average over the  $|JM\rangle$  sublevels, the  $z$  axis is chosen to be along the surface normal,  $P_2$  is a second-order Legendre polynomial, i.e.,  $P_2(\cos \theta) = (3\cos^2 \theta - 1)/2$ , and  $\theta$  is the angle between  $\mathbf{J}$  and the surface normal. Thus, the value of  $A_{0+}^{(2)}$  ranges between  $+2$  and  $-1$  and equals  $0$  for an isotropic spatial distribution of  $\mathbf{J}$  vectors.

The scattering of  $N_2$  from Ag(111) illustrates this beam-surface polarization technique. Sitz et al. [34] have found that for this system the values of  $A_{0+}^{(2)}(J)$  approach closely the limiting value of  $-1$  for large  $J$  values ( $J > 12$ ). Indeed, they report that the average of  $A_{0+}^{(2)}$ , weighted by the population of each  $J$  level, is

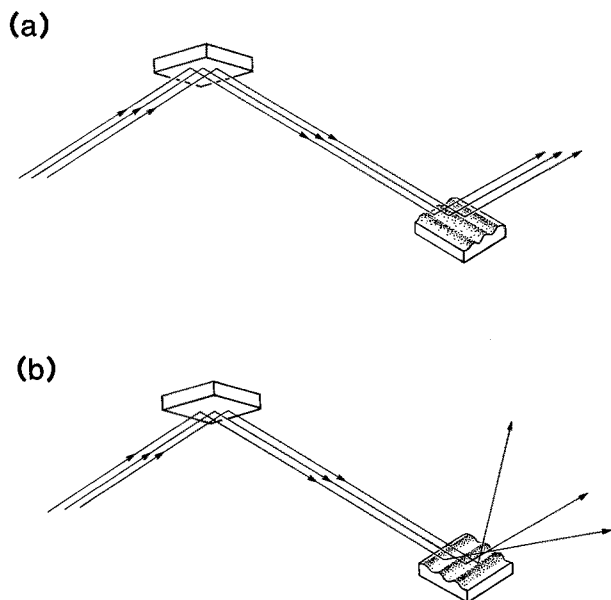
$$\langle A_{0+}^{(2)} \rangle = -0.75 \quad (2)$$

at specular scattering. To appreciate this degree of alignment, suppose that this value of  $A_{0+}^{(2)}$  applies to the rotational level  $J=15$  (actually  $A_{0+}^{(2)}(15)$  is somewhat larger). This level has  $2J+1=31$  different  $M$  sublevels which for an isotropic distribution would be equally populated. If it is assumed that the  $M$  sublevel distribution may be represented by a Gaussian, then  $A_{0+}^{(2)} = -0.75$  implies a full width at half maximum of 7 sublevels, i.e.,  $M$  peaks at  $M=0$  but range from  $M=+3$  to  $M=-3$  at FWHM. Using the semiclassical relation,

$$\cos \theta = \frac{M}{[J(J+1)]^{1/2}}, \quad (3)$$

this value of  $A_{0+}^{(2)}$  corresponds to  $\mathbf{J}$  making an angle with the surface normal of  $90 \pm 12^\circ$ .

Once a polarized beam is prepared by the first surface scattering event, the second surface scattering event may be chosen at will. For example, Fig. 5 pictures the different possible scattering behavior when a beam of aligned molecules strikes a surface either



**Fig. 5a and b.** The proposed molecular double bank shot experiment in which a polarized beam, prepared by scattering an incoming beam from the first surface, strikes a second surface having a different surface geometry depending upon its position. Shown is an aligned beam incident on a surface with ridges: (a) along the direction of ridges; and (b) perpendicular to the direction of ridges

along or against a set of ridges characteristic of a (110) surface. Perhaps one of the most interesting studies might be the variation in sticking coefficient for the two different surface geometries shown in this figure [37]. This could be readily monitored by temperature programmed desorption of the second surface after the incident beam has been blocked. The second surface need not be structured to make the double scattering process quite interesting. An example would be a beam of oriented molecules striking a flat surface where the degree of orientation is chosen to be positive or negative, analogous to a table tennis ball striking the playing surface with top or back spin. The possibilities are numerous. It might be hoped that Otto Stern would have enjoyed seeing the outcome of this double surface scattering experiment, the molecular double bank shot.

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36. By alignment we mean the preferential population of magnetic sublevels  $+M$  and  $-M$  as opposed to  $+M'$  and  $-M'$ ; this is equivalent to molecules in a state  $J \neq 0$  having a preferred plane of rotation. By orientation we mean the preferential population of  $+M$  as opposed to  $-M$ ; this is equivalent to molecules in a state  $J \neq 0$  having a preferred sense of rotation. Thus, alignment refers to the even moments of the spatial distribution of  $\mathbf{J}$  vectors, orientation to the odd moments. In general, a molecular ensemble can be both aligned and oriented
37. I thank Melissa A. Hines for suggesting this idea