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Large Rotational Polarization Observed for H_2, D_2, and HD Scattered from LiF(001)

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Molecular angular-momentum polarization produced in gas-surface collisions is investigated by the magnetic field effect on a Knudsen flow. The effects for H_2 isotopes scattered by LiF(001) surfaces are found to be 2 to 3 orders of magnitude larger than previously observed for metal surfaces. This is attributed to the large corrugation of the LiF crystal face, since the polarization type involved is produced by in-plane forces. Both first- and second-rank polarizations ("orientation" and "alignment") are observed, the production matrix elements being of order 10^{-1} to 10^{-2}.

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In the study of molecule-surface interaction, direct information on the nonisotropic forces acting on a molecule during collisions is obtained from the behavior of the molecular angular momentum. In addition to the rotational energy distribution of the outgoing molecules,[1] data on the orientational distribution of their angular momenta can be a fruitful source of information. Indeed, since angular momentum is a vector quantity, such data may produce more detailed information on molecule-surface interaction than do measurements on the scalar rotational energy distribution. Anisotropic distributions of angular momentum may in general be called "polarizations." They can be expressed in terms of the multipole moments in angular-momentum space of the distribution, in which the odd moments describe orientation and the even moments alignment.[2]

One experimental approach to the study of such polarizations is by means of molecular beams in combination with some optical detection scheme such as laser-induced fluorescence or multiphoton ionization. To date, only two such experiments have been performed. The system NO/Ag(111) was studied by Luntz, Kleyn, and Auerbach,[3,4] and the system N_2/Ag(111) by Sitz, Kummel, and Zare.[2,5] In both experiments large alignments were observed which can be interpreted as rotational excitation at a flat surface with conservation of the initial (low) m_J value, by forces acting perpendicular to the surface[3,4,6]; here m_J is the z projection of the rotational quantum number. In addition, in the latter experiment[2] also orientational effects were observed which require the action of tangential or in-plane forces during the collision. Such in-plane forces, which change the parallel velocity component of the colliding molecule, can arise from surface corrugation.

A quite different experimental approach for the investigation of those polarizations which are caused by in-plane forces is to study their role in a free molecular or Knudsen flow between two parallel surfaces. This is achieved by our scrambling the polarization through precession of the molecular angular momentum **J** in an external magnetic field. This technique is applicable to any molecular species, since each rotating molecule carries a magnetic moment $\boldsymbol{\mu} = g\mu_N \mathbf{J}/\hbar$, where μ_N is the nuclear magneton and g the molecular Landé factor ($g = 0.88$ for H_2, 0.66 for HD, and 0.44 for D_2).

The physical picture of this effect is as follows. During a collision with a surface, a molecule can convert part of its parallel motion into angular momentum. During the next collision at the opposite surface, the reciprocal effect will take place; the angular momentum will influence the parallel motion, much like a spinning tennis ball. If, during the free-flight time in between the two collisions, the direction of the angular momentum is changed by precession, the outgoing velocity at the second collision is also changed. This will influence the flow of the gas as a whole. Note that, even in case the trajectories of the molecules closely resemble a random walk, this process is not confined to the first few collisions: Continuity requires a net forward velocity to persist at any position downstream, driven by the density gradient. Note also that molecules which have been temporarily trapped, even if they would be polarized upon desorption,[7] do not contribute since their outgoing velocity distribution can be assumed to be symmetric along the surface normal and to carry no memory for the flow direction.

The kinetic theory of this effect is well established for the case of classical rigid rotors.[8,9] Exploratory experiments[10,11] for various gases on surfaces of Au, Pt, and mica, which were presumably dominated by adsorbates, could be fairly well described by this theory. The effects were found to be quite small, the relative change in the Knudsen flow being only on the order 10^{-5} to 10^{-4}.

However, the production of the relevant polarizations depends on in-plane forces acting during the molecule-surface collisions. In fact, the responsible matrix elements[9] of the surface scattering operator can be shown to vanish if the parallel velocity is conserved. Such is the case for collisions with a smooth surface. In contrast, for particles colliding with a sinusoidal surface, the average change in the parallel momentum is found to be proportional to the square of the corrugation amplitude. One should therefore expect larger effects for surfaces having a large corrugation amplitude.

The (001) plane of LiF provides such a surface. From molecular-beam studies[12] it is known to have a corrugation amplitude for thermal particles of about 0.3 Å in the [100] direction. In addition, the trapping probability is small, the attractive potential well being only about 40 meV for H_2 isotopes.[13] Therefore, we constructed a flow channel (length 20 mm, width 10 mm, gap 0.17 mm) from LiF(001) faces with two 0.17-mm-thick Pt wires serving as spacers. It was assembled in a dry N_2 atmosphere at 900 K with a mixture of LiF and PbF_2 used as solder. Details of the construction will be given elsewhere.[14] No further treatment was given to the channel before evacuation of the system and introduction of a gas flow. In order to assess the possible role of contaminants like adsorbed H_2O in the experiment, preliminary measurements were performed for HD at elevated temperatures up to 690 K. Since the data showed only gradual and moderate changes, the role of adsorbates—if any—is expected to be small. This is consistent with the observations by Estel *et al.*,[15] who found adsorption of H_2O on LiF only on cooled surfaces below 200 K, the adsorption energy being in the 200-meV range.

In the experiment, a gas flow at pressures around 1 Pa or 10^{-2} Torr was established through the channel, yielding Knudsen numbers (ratio of mean free path to gap thickness) around 50. Magnetic fields up to $B=2.2$ T were applied. This produces maximum precession angles $\omega\tau$ on the order of 10; here $\omega=gB\mu_N/\hbar$ is the precession frequency and $\tau=b(m/2kT)^{1/2}$ an average flight time across the gap (with $b=0.17$ mm). The field could be oriented parallel to the flow, $\mathbf{B}=(B_x, 0,0)$, and perpendicular to both flow and surface normal, $\mathbf{B}=(0,B_y,0)$ (cf. coordinate system in Fig. 1).

The resulting changes in the flow at constant pressure drop, $\delta\Phi/\Phi$, are given in Fig. 1 as functions of precession angle. The effects are found to be 2 to 3 orders of magnitude larger than those observed earlier for Au-coated surfaces,[11] the relative change in flow now being on the order of 1%. This means that the matrix elements describing production of polarization are on the order 10^{-1}, since squares of these matrix elements determine the magnitude of $\delta\Phi/\Phi$. The physical reason for this is that two successive collisions have to be considered: a "polarizing" collision and an "analyzing" collision (see above).

A second feature seen from Fig. 1 is that H_2 shows the largest effect and HD the smallest. This is somewhat unexpected, since for HD rotational excitation both in gas phase[16] and in collisions with metal surfaces[17] is known to be much stronger than for the homonuclears. This is partly due to the shift of its center of mass away from the H—D bond center, and partly to the selection rule $\Delta J=\pm 1$ as opposed to $\Delta J=\pm 2$ for H_2 and D_2. In addition, one should note that H_2 has the largest rota-

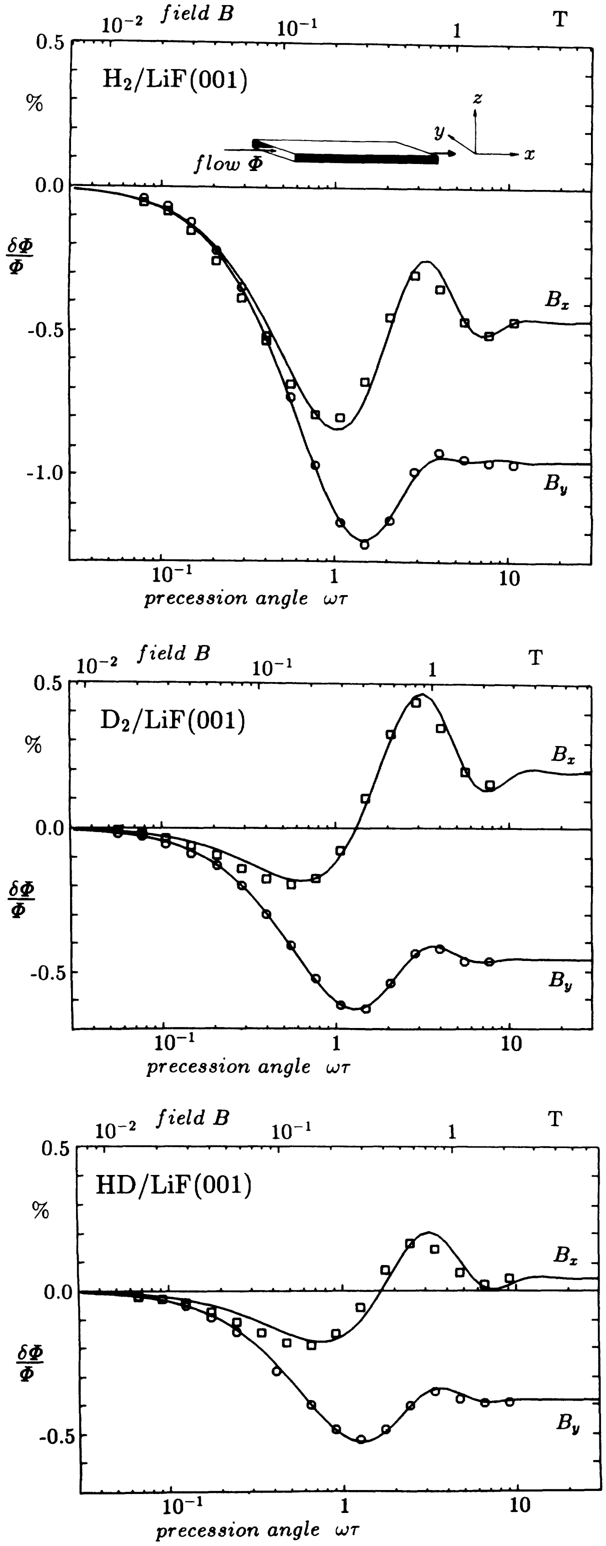

FIG. 1. Experimental results for the field-induced change in the flow with the field along the x and y axes. The curves drawn through the data are superpositions of $F(\omega\tau)$ and $-F(2\omega\tau)$, with the weight of the two contributions chosen such as to yield the best fit.

tional level splitting of the three, with $\hbar^2/2Ik = 85$ K.

In order to deconvolute the data into contributions from individual polarizations, we turn to the theoretical framework of Ref. 9. It should be stressed at this point that, since the surface scattering operator is a scalar, the Curie principle requires that a particle flow along a surface, having a vector character, can generate only polarizations (in the combined velocity-angular-momentum space) which are true vectors. In the kinetic description of Ref. 9, only the four simplest polarizations were considered, viz., two of first rank in **J** ("orientation") and two of second rank ("alignment"). The **J**-dependent parts are proportional to the real parts of spherical harmonics Y_{lm} with $l=1$ and 2, and $|m|=0$ and 1. The resulting polarizations are listed in Table I. A physical picture can be found in Refs. 9 and 11. Note that, as in Ref. 9, we have switched to normalized peculiar velocity **v** and angular momentum **J** through division by $(2kT/m)^{1/2}$ and $(2IkT)^{1/2}$, respectively. Identification of these polarizations in the experiment can be achieved by our making use of the specific behavior of their contributions to the field effect. First of all, polarizations of first rank in **J** produce $\delta\Phi/\Phi > 0$ (i.e., the flow will increase if the field is switched on) while polarizations of second rank will produce $\delta\Phi/\Phi < 0$. In addition, the dependence of $\delta\Phi/\Phi$ upon precession angle $\omega\tau$ is for first-rank polarizations always given by the standard function $F(\omega\tau)$:

$$F(\omega\tau) = 2\int_0^\infty v_z \exp(-v_z^2)[1-\cos(\omega\tau/v_z)]dv_z, \quad (1)$$

where v_z represents the dimensionless z velocity of a molecule. For second-rank polarizations, this dependence can also be $F(2\omega\tau)$, viz., for field orientations which produce a precession in a plane where the polarization has C_2 symmetry (see, e.g., Ref. 11). This behavior is summarized in Table I.

The experimental data can now be compared with superpositions of $F(\omega\tau)$ and $-F(2\omega\tau)$, with $\omega\tau$ fixed by the known values of field strength and gap width. From Fig. 1 it is seen that the data for $\mathbf{B} = (0, B_y, 0)$ are fitted extremely well by this theoretical description, especially for D_2 and HD which show an almost pure $-F(2\omega\tau)$ behavior. These data reveal the strength of the production of second-rank polarization or alignment. The data for $\mathbf{B} = (B_x, 0, 0)$ are reasonably well described by a superposition of $F(\omega\tau)$ and $-F(2\omega\tau)$. They show that also first-rank polarization, viz., orientation of type J_y, is produced and even dominates in the case of D_2.

TABLE I. Four types of polarization in the combined velocity-angular-momentum space which can be produced in a free molecular flow between parallel plates (see Fig. 1 for geometry) and their contributions to the field effect $\delta\Phi/\Phi$ as a function of $\omega\tau$ [cf. Eq. (1)]. Note that the polarizations are actually x components of true vectors (Ref. 9), e.g., $J_y = (\mathbf{J}\times\mathbf{n})_x$ with **n** the surface normal.

Type of polarization	Contribution for field orientation shown B_x	 B_y
$v_y J_z$	$\propto F(\omega\tau)$	$\propto F(\omega\tau)$
J_y	$\propto F(\omega\tau)$	0
$v_x(3J_z^2 - J^2)$	$\propto -F(2\omega\tau)$	$\propto -F(2\omega\tau)$
$J_x J_z$	$\propto -F(\omega\tau)$	$\propto -F(2\omega\tau)$

By use of both the $F(\omega\tau)$ and the $F(2\omega\tau)$ contribution from either curve, all four polarizations from Table I can now be determined. The result of such an analysis is that the second-rank polarizations produced for H_2, D_2, and HD on LiF are almost exclusively of the alignment type, $v_x(3J_z^2 - J^2)$. The intuitive classical picture[9] which may be associated with this polarization is that the molecules change their forward motion upon impact, while aligning their angular momentum vectors with respect to the surface normal ("helicopter motion"). The absolute value of the matrix element of the scattering operator $\hat{P}$ is found to be $\langle v_x(3J_z^2 - J^2) | \hat{P} v_x\rangle = 8.4\times10^{-2}$ for H_2, 6.3×10^{-2} for D_2 and 5.4×10^{-2} for HD. Analogously, the first-rank polarization observed is found to be almost exclusively of the orientation type J_y. The corresponding intuitive classical picture is that of a tennis ball obliquely hitting a rough surface.[11] The magnitude of the corresponding matrix element is found to be $\langle J_y | \hat{P} v_x\rangle = 3.3\times10^{-2}$ for H_2, 3.9×10^{-2} for D_2, and 3.2×10^{-2} for HD.

The actual degree of alignment and orientation in a given flow can be deduced from the above by multiplication of the matrix elements by flow velocity $\bar{v}_x$ divided by average thermal velocity $\bar{v}$, e.g., $\langle J_y\rangle_{\text{n.e.}} \approx 4\pi^{-1/2}\langle J_y | \hat{P} v_x\rangle \bar{v}_x/\bar{v}$. Here, the nonequilibrium average $\langle J_y\rangle_{\text{n.e.}}$ is taken over the half space of molecules leaving a surface. Note that for the equilibrium average one has $\langle J_y\rangle = 0$; in the limit of perfect orientation of all angular momenta in the $+y$ direction one finds, using the above normalization, $\langle J_y\rangle = \frac{1}{2}\sqrt{\pi}$ if the distribution over rotational energy is assumed to remain Maxwellian.

These data show the need for detailed quantum-mechanical molecular-dynamics simulations of light diatoms colliding with a corrugated surface. So far, surface corrugation was found to decrease the quadrupole type of alignment already produced at a flat surface,[18] or to be of minor importance.[19,20]

Several conclusions can be drawn from these results. First, they demonstrate that relatively large polarizations of this type, which depend entirely on the existence of in-plane forces, can be produced for diatomic molecules at highly corrugated surfaces like LiF(001). This includes alignment with symmetry around the surface normal ("helicopter type") as well as orientation perpendicular to both surface-normal and incoming velocity vector ("tennis-ball type"). Second, they show that the off-center rotation of HD plays a much smaller role in the nonspherical interaction responsible for these polarizations than one might expect. Next, they show that the kinetic theory for this effect, which was worked out for classical linear molecules, gives also a surprisingly good description of the behavior of H_2 isotopes. In addition, they show that in the kinetic description of ordinary Knudsen flow for polyatomic molecules, drag contributions arising from polarization may not be negligible if the surface of the duct is highly corrugated. Finally, these experiments suggest that it may be feasible to produce molecular beams having an appreciable angular-momentum polarization by use of appropriate nozzles.

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[1] For a review see, e.g., J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. **4**, 1 (1984).

[2] G. O. Sitz, A. C. Kummel, and R. N. Zare, J. Chem. Phys. **87**, 3247 (1987).

[3] A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, Phys. Rev. B **25**, 4273 (1982).

[4] A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, Surf. Sci. **152**, 99 (1985).

[5] G. O. Sitz, A. C. Kummel, and R. N. Zare, J. Vac. Sci. Technol. A **5**, 513 (1987).

[6] J. G. Lauderdale, J. F. McNutt, and C. W. McCurdy, Chem. Phys. Lett. **107**, 43 (1984).

[7] Such rotational alignment in desorption was recently observed by D. C. Jacobs, K. W. Kolasinski, R. J. Madix, and R. N. Zare, J. Chem. Phys. **87**, 5038 (1987), and by L. V. Novakoski and G. M. McClelland, Phys. Rev. Lett. **59**, 1259 (1987).

[8] V. D. Borman, S. Yu. Krylov, B. I. Nikolaev, V. A. Ryabov, and V. I. Trojan, Zh. Eksp. Teor. Fiz. **79**, 1787 (1980) [Sov. Phys. JETP **52**, 904 (1980)].

[9] H. F. P. Knaap and I. Kuščer, Physica (Amsterdam) **104A**, 95 (1980).

[10] J. J. G. M. van der Tol, S. Yu. Krylov, L. J. F. Hermans, and J. J. M. Beenakker, Phys. Lett. **99A**, 51 (1983); J. J. G. M. van der Tol, L. J. F. Hermans, S. Yu. Krylov, and J. J. M. Beenakker, Physica (Amsterdam) **131A**, 545 (1985), and **134A**, 216 (1985), and **139A**, 28 (1986).

[11] L. J. F. Hermans, J. J. G. M. van der Tol, and J. J. M. Beenakker, J. Chem. Phys. **84**, 1029 (1986).

[12] G. Boato, P. Cantini, and L. Mattera, Surf. Sci. **55**, 141 (1976).

[13] G. Boato, P. Cantini, and L. Mattera, J. Chem. Phys. **65**, 544 (1976).

[14] R. Horne *et al.*, to be published.

[15] J. Estel, H. Hoinkes, H. Kaarmann, H. Nahr, and H. Wilsch, Surf. Sci. **54**, 393 (1976).

[16] P. W. Hermans, L. J. F. Hermans and J. J. M. Beenakker, Physica (Amsterdam) **122A**, 173 (1983).

[17] J. P. Cowin, Chein-Fan Yu, S. J. Sibener, and L. Wharton, J. Chem. Phys. **79**, 3537 (1983).

[18] R. J. Wolf, D. C. Collins, and H. R. Mayne, Chem. Phys. Lett. **119**, 533 (1985).

[19] C. Y. Lee, R. F. Grote, and A. E. DePristo, Surf. Sci. **145**, 466 (1984).

[20] S. Saini, D. A. Dows, and S. H. Taylor, Chem. Phys. **90**, 87 (1984).