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<sup>5</sup>K. L. Kompa and co-workers have recently studied multiphoton dissociation with crossed molecular and laser beams. They have found a 30% depletion of SF<sub>6</sub> in the beam by the laser field. However, limited by

their apparatus, they have not been able to carry out the type of measurements reported in this Letter. See K. L. Kompa, in *Proceedings of the Conference on Laser Chemistry*, Steamboat Springs, Colorado, February, 1976 (to be published).

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## Observation of High-Resolution Differential Cross Section of Polarized, Rotationally State-Selected LiF on Ar†

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We report high-resolution differential cross sections at thermal energy for polarized, rotationally state-selected LiF on Ar. They were 2–8% larger with LiF in the  $J = |M| = 1$  orientation along the relative velocity than in the  $J = 1$  unpolarized state. The differential cross section in the present case is much more sensitive to change in polarization than is the total cross section. The high-frequency oscillations of the differential cross sections were found substantially independent of  $J$  when the present  $J = 1$  data were compared with non-state-selected data for  $\bar{J} = 15$  or  $\bar{J} = 25$ .

The measurement of the variation of total scattering cross section with polarization in state-selected beams has given information about the angular dependence of intermolecular potentials.<sup>1,2</sup> However, the effects of change of polarization upon the received signal are small. Because long integrating times are necessary, it is difficult to obtain the velocity dependence of the difference in total cross section due to polarization, which gives further information about the radial dependency of the angular dependent terms in the intermolecular potential. This laboratory has recently performed measurements of the velocity variation of the differential cross section for atom-atom<sup>3</sup> and atom-molecule<sup>4</sup> scattering. LiF-Ar was studied<sup>4</sup> in the thermal energy range under conditions of very high resolution in which all features of the quantum mechanical scattering were observable, although the rotational states of the molecule were thermally distributed. Observation of damped high-frequency (diffraction) and low-frequency (rainbow) oscillations<sup>5</sup> permitted a determination of the spherically averaged potential and some characteristics of the angular dependent potential. The present experiments combine the observational advantages of both state selection and high-resolution differential

cross sections.

The use of a seeded high-temperature supersonic source to cool the LiF beam translationally and rotationally, and the use of quadrupole fields to provide finite-aperture ( $f/100$ ) optics made possible the observation of the differential cross section of a state-selected molecular beam at intensities of about  $\frac{1}{5}$  that of a non-state-selected molecular beam previously used and with no sacrifice in geometrical angular resolution. A supersonic Ar jet carried 0.5-Torr superheated LiF as it expanded from 300 Torr at 1750 K from an indirectly heated graphite oven through a 0.15-mm thin orifice. It was skimmed by a 50° full angle, 0.5-mm-diam truncated cone.<sup>6</sup> Rotational and translational temperatures ranged from 25 to 85 K. Differential pumping was provided by a 100-1/sec booster and by 4200- and 200-1/sec diffusion pumps, sequentially, to a pressure of  $1 \times 10^{-7}$  Torr in the first refocuser chamber. The chamber containing the second refocuser and the scattering apparatus was pumped by a 600 1/sec ion pump supplemented by liquid hydrogen cryopumping and Ti sublimation pumping to a pressure of  $3 \times 10^{-8}$  Torr. The state selectors were two 180° refocusing "three-quarter" quadrupoles together with apertures for velocity selection (8.5% stan-

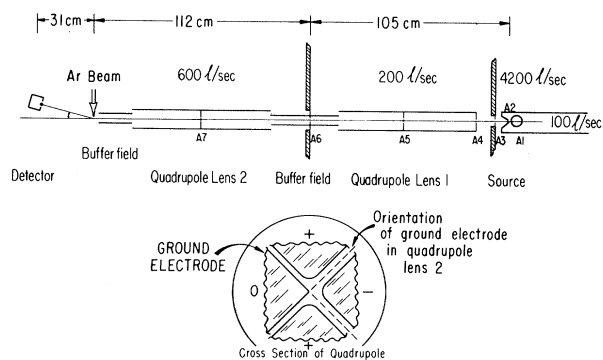


FIG. 1. Schematic of the apparatus. Dimensions of apertures (mm):  $A1=0.15$ ;  $A2=0.5$ ;  $A3=3.5$ ;  $A4=1.25$ ;  $A5=2.5$  o.d.,  $1.25$  i.d.;  $A6=0.5$ ; and  $A7=A5$ .

dard deviation) and elimination of all other states and background LiF (less than  $2 \times 10^{-3}$  of the refocused  $J=1, M=0$  beam). Additional buffer electrodes and the use of dielectric material for beam stops eliminated nonadiabatic transitions. A schematic is given in Fig. 1. The fourth pole was replaced by a ground electrode congruent to the two perpendicular zero-potential surfaces. It prevented trajectories from crossing the lens axis, eliminating "higher harmonics," and formed a convenient base for mounting intermediate beam stops.

Incoming LiF and Ar beams had velocities of  $1.4$  and  $3.7 \times 10^5$ , and  $5.6 \times 10^4$  cm/sec, respectively, intersecting at  $90^\circ$ . The cross beam and analyzing apparatus was substantially the same as described previously<sup>3,4</sup> with geometrical angular resolution of about  $0.05^\circ$ .

The differential cross sections weighted by  $\theta^2$  for scattering of the  $J=1$  state of LiF on Ar are displayed in Fig. 2 for two polarization conditions, for angles from  $0.4$  to  $3^\circ$ . In one condition only the  $M=0$  polarization in an electric field perpendicular to the plane of the crossed incoming beams was present, producing  $J=1, |M|=1$  polarization along the relative velocity vector,<sup>5</sup> while in the other an unpolarized  $J=1$  state was present. The difference in the  $\theta^2$ -weighted differential cross section between these two (polarized and unpolarized) initial states is also displayed.

The most important result of this experiment is that there is a substantial difference signal. Since data of the present sort are subject to both random and systematic errors, it is appropriate to discuss the evidence that the differences in cross section due to polarization have the significance stated. The estimated standard deviation due to shot noise of a single point was  $1.3\%$  on the average between  $0.5$  and  $2^\circ$ , while the observed stan-

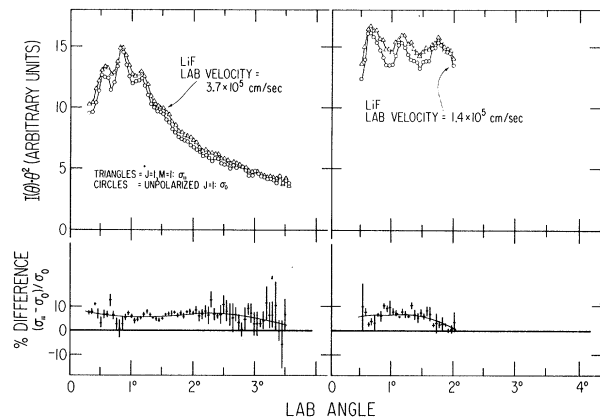


FIG. 2. Laboratory  $\theta^2$ -weighted differential cross section of LiF on Ar. Polarized LiF beam is in  $(J, M) = (1, 0)$  in electric field perpendicular to plane of intersecting beams, equivalent to  $(J, |M|) = (1, 1)$  along relative velocity. Unpolarized LiF beam is in  $J=1$  state. Error bars are 1 standard deviation.

dard deviation as measured by reproducibility from one scan to another was  $1.5\%$ . (There is some variation of these numbers over the range of angles observed due to varying signal levels.) In subtracting the two differential cross sections on a point by point basis the standard deviation is  $\sqrt{2}$  larger, i.e.,  $2.1\%$ . The percent difference in differential cross section between initially polarized and unpolarized states of laboratory angle was least-squares-fitted to various orders of Chebyshev polynomials. It was found that the fit was not improved beyond order  $n=3$ , and the resulting standard deviation of a point from this  $n=3$  fitted curve was approximately  $2.1\%$ . By this smoothing technique, the expected standard deviation of the true value of the differential cross section difference is smaller than  $2.1\%$  by the factor  $[(n+2)/NV]^{1/2}$ , where  $NV$  is the number of angles of observation  $\sim 30$ . Thus if the data were subject to random errors only, the fitted curves would have a standard deviation of  $0.9\%$ . Since the fitted curve has a magnitude ranging from  $2$  to  $8\%$ , the difference in the differential cross section is determined with a signal-to-standard-deviation ratio of  $2$  to  $8$ . It is also significant that substantially all the differences in differential cross section data are positive.

The evidence that the difference data are not dominated by systematic error is the following: (1) The difference in differential cross section disappears as the quantizing field in the collision region is turned off. Yet, if the field is increased beyond  $500$  V/cm, the effect does not further in-

crease. (2) At differing primary beam velocities the effect has a different angular dependence.

(3) When the target gas is not present, no effect is seen. These tests are persuasive that the effect is not due to a geometrical artifact of the apparatus, deflections of the primary beam due to field inhomogeneities, interactions with background gas, etc.

An interpretation of the effect of polarization that is consistent with previous measurements on LiF-Ar is that the small-angle scattering is due, in great measure, to a long-range attractive  $r^{-s}$  potential, where  $s=6$ , and which consists of spherical and angular dependent  $P_2(\cos \theta)$  terms of approximately equal size. Using the high-energy<sup>5</sup> approximation for the intermolecular energy, and classical mechanics to calculate the trajectories, a much smaller difference in the differential cross section ( $\sim 2\%$ ) was calculated than was observed. However, an approximate quantum mechanical calculation<sup>4</sup> using a superposition of spherical model potentials showed that very much larger changes of the differential cross section with initial polarization can occur. The results possessed broad angular regions of the differential cross section where the change of cross section with polarization was either positive or negative. These regions were associated with angular shifts of the first order and super-numerary rainbows, and the largest changes occurred as expected at the sides of the rainbow peaks. (It had been previously shown that there was a marked effect of the angular dependent part of the potential upon the location of rainbow features.) A more complete interpretation is needed which includes the undulations associated with shifts in rainbow features and changes in the differential cross sections that vary less rapidly with angle. Both effects are discernible in the present experiments.

In the range of experimental angles, three or more cycles of high-frequency oscillation were observed. The location and amplitude of the high-frequency features of the differential cross sections resembled those expected from previously<sup>4</sup> observed oscillations at the same relative velocity, in which the LiF had not been rotationally state-selected and had mean rotational  $J$  of 15 or 25. It had been previously concluded that within this range of rotational states this feature of the high-resolution differential cross section was substantially independent of  $J$ . The present results extend the  $J$  independence down to  $J=1$  for the angular range  $0.4-3^\circ$ . The radius of the "loc-

us of  $r_m$ ", where  $r_m$ <sup>4</sup> is the center-of-mass separation at the potential minimum, shows small variation with orientation. The spacing of the high-frequency diffraction oscillations observed in these experiments is, to a good approximation, inversele proportional to this radius. Variation of this radius with orientation would show up directly in variation of the spacing of these oscillations with  $|M|$ .

It is interesting to compare this technique to that of variation of total cross section with polarization. The total scattering cross section does not display such a large effect of polarization. Furthermore, the technique of anisotropic glories<sup>7</sup> is less applicable to systems with sufficiently large anisotropy in the intermolecular potential since glory interferences in the total cross section will be substantially reduced by a variety of possible rotational transitions. Small nonglory contributions<sup>2b</sup> occurring at large impact parameters will remain to contribute to the effect of polarization on the total cross section. The typical impact parameter and the immunity against rotational transitions will be larger for the rainbows than for the glory interference features. Shifts of unquenched rainbows with consequential enhancement of the effect of polarization upon the differential cross section will persist to higher degrees of anisotropy in the intermolecular potential. In the present case the anisotropy of the intermolecular potential nearly completely quenches the glory features<sup>8</sup> of the total cross section but not the rainbow features of the differential cross section.<sup>4</sup> Observations of the present sort then give information about the nature of the angular dependence of intermolecular potentials because of their great sensitivity to anisotropy. The use of other selected initial states should clarify the nature of the angular variation of the potential.

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## Nucleation of Solid He<sup>4</sup> Interfaces between Grafoil and High-Pressure Liquid He<sup>4</sup>

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We report the continuous growth, on a microscopic scale, of solid He<sup>4</sup> from superfluid He<sup>4</sup> caused by its substrate interaction with Grafoil. The measurements indicate the presence of a surface solid layer whose thickness varies from 8 Å to more than 30 Å from the Grafoil substrate as the bulk solidification curve is approached. The results are in good agreement with a theory based on the van der Waals attraction between the He<sup>4</sup> and the substrate.

First-order phase transitions, such as solid-liquid transitions, are commonly thought of and dealt with as purely bulk phenomena. It is appreciated that such transitions are probably usually nucleated in some fashion by impurities or walls, but details of this process have never before, to the authors' knowledge, been examined in careful detail.<sup>1</sup> What we report here are the first measurements of the continuous growth, on a microscopic scale, of a solid as the pressure approaches that of the solidification curve. The system studied is superfluid He<sup>4</sup> in contact with graphite in the form of Grafoil.<sup>2</sup> He<sup>4</sup> was chosen for convenience, but we must strongly emphasize that the basic phenomena studied are much more general in that they are qualitatively independent of both substrate and fluid. The data are analyzed in terms of a theory based on the van der Waals attraction between the fluid and the substrate, and good agreement between theory and experiment is obtained.

One additional interesting effect is observed. Measurements of the pressure  $P$  in the system are along isopycnals, i.e., at constant He<sup>4</sup> number  $N$  and (essentially) constant He<sup>4</sup> volume  $V$ , the temperature  $T$  being varied. Along two such isopycnals, were the surface solid behaving like the bulk form, there would be a transition from the bcc phase to the hcp phase. Comparison of the theory to experiment strongly indicates that

the solid film being formed remains in a single phase, taken to be the bcc phase since this is the natural one over most of the temperature range. A definitive study, using neutron-scattering techniques,<sup>3</sup> would be most useful in examining this metastable behavior.

The basic physical ideas involved in our work are relatively simple. The substrate provides an external potential in which the He<sup>4</sup> moves. In equilibrium the temperature  $T$  and He<sup>4</sup> chemical potential  $\mu$  are constant throughout the system, the local He<sup>4</sup> number density  $n(\vec{r})$  adjusting itself so that this is indeed the case.<sup>4</sup> Letting  $U(\vec{r})$  be the external potential, the condition for equilibrium is  $\mu = \mu_0\{n\} + U(\vec{r})$ . Very generally,  $\mu_0\{n\}$  must be regarded as a *functional* of  $n(\vec{r})$  (and a function of  $T$ ). Our analysis will be predicated on the assumption that the function is well-approximated by a *local* function of  $n(\vec{r})$  given by the bulk He<sup>4</sup> chemical potential  $\mu_0(n(\vec{r}), T)$  for the appropriate bulk phase of He<sup>4</sup> in the absence of any external effects. It is then convenient to regard  $\mu_0$  as a function of the local pressure  $P(\vec{r})$  and  $T$  in place of the variable pair  $n(\vec{r})$  and  $T$ . The equilibrium condition then informs us that, on moving a small distance in the system, changes in  $U(\vec{r})$  are related to changes in  $P(\vec{r})$  via

$$dU(\vec{r}) = -(\partial\mu_0/\partial P)_T dP(\vec{r}) = -[1/n(\vec{r})]dP(\vec{r}). \quad (1)$$

Here the second equality follows from the local