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DIFFERENTIAL COLLISION CROSS-SECTION MEASUREMENTS IN THE ELASTIC SCATTERING OF LIGHT IDENTICAL MOLECULES: HELIUM

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Differential collision cross sections in the elastic scattering of helium beams are reported. A supersonic room-temperature primary beam and a multichannel low-temperature secondary beam have been used. The first quantum oscillation has been resolved. The results are compared with cross sections computed numerically, describing the interaction by means of potentials previously reported in the literature. Computed predictions are in fair agreement with experimental results.

Molecular-beam scattering experiments are now a well established technique for the study of intermolecular forces.[1] Because of experimental difficulties, the most precise experiments to date have been made on systems in which at least one of the scattering partners is an alkali.[1,2] Nevertheless, in order to compare the results with information gathered from statistical-mechanical theories of bulk properties, scattering experiments of good energy and angular resolution are needed on systems other than alkalis, in particular noble gases.

As far as we know only two differential collision cross-section measurements of nonalkali systems have been performed with beams of reduced energy spread. In the first, Bickes and Bernstein[3] resolved the rainbow structure of the Ar-N_2 system. In the second Winicur et al.[4] resolved a few quantum oscillations in the differential cross section of the D_2-N_2 system. The use of different elements in the primary and secondary beam, which makes the comparison with bulk properties less straightforward, and the particular choice of the systems was, in both experiments, probably dictated by the noise problem at the detector, a mass spectrometer in both cases.

In the present Letter we report differential collision cross-section measurements on helium performed using a novel technique which has several advantages arising from the use of very low temperatures.

The choice of the system has been made taking into account that the helium atom is "simple" from the point of view of ab initio calculations of intermolecular forces, and its bulk properties have been extensively studied because of their practical interest and unusual quantum properties. The necessary low relative velocity spread has been achieved by keeping the secondary beam source at 40°K and, as in previous investigations, by the use of a supersonic primary beam.[5] The noise at the detector has been reduced by using a low-temperature bolometer,[6] to determine the flux of molecules from the flux of energy, and by placing cold shields around the detector itself.

A schematic diagram of the apparatus is shown in Fig. 1. A chopped (30 Hz), room-temperature, supersonic primary beam with a calculated Mach number >15 was crossed at right angles (at about 7 cm from the skimmer) by a secondary beam produced by a 40°K multichannel glass capillary source. The dimensions of the scattering volume were approximately $(3\times10^{-2})(5\times10^{-2})(2\times10^{-1})$ cm^3. The liquid-helium-cooled bolometer detector (width 0.04 cm, height 0.3 cm, responsi-

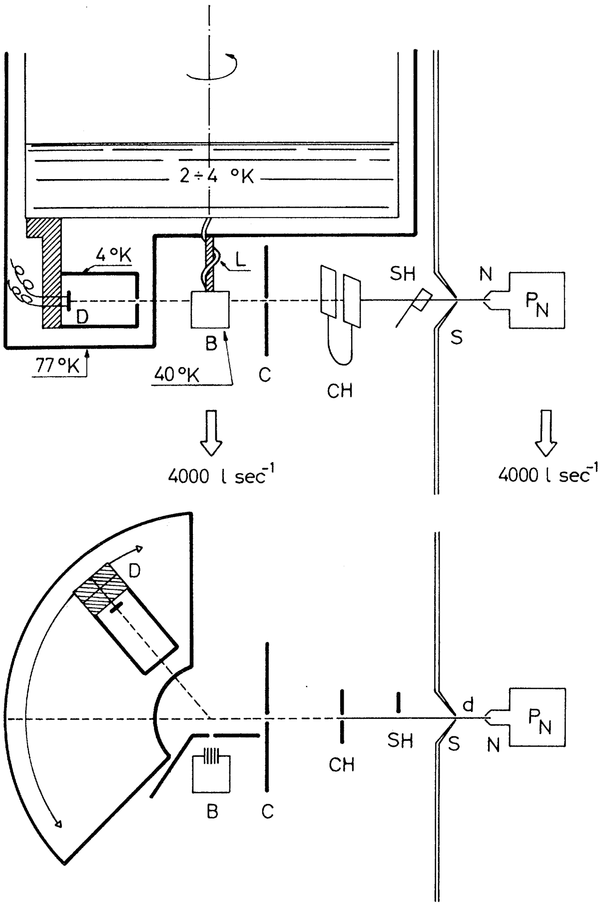

FIG. 1. Schematic diagram of the apparatus. N, nozzle (diam 2×10^{-3} cm); S, skimmer (diam 4×10^{-2} cm); d, nozzle-skimmer distance (typically 0.4 cm); P_N, nozzle stagnation pressure (typically 30 atm); SH, beam shutter; CH, beam chopper; C, collimator; B, secondary source; L, copper thermal link; D, bolometer detector.

vity 7×10^5 V W^{-1}, noise equivalent power 10^{-13} W Hz$^{-1/2}$) could be rotated at 5.8 cm from the scattering center in the plane of the two beams. Typical background pressures were 10^{-4} Torr and 7×10^{-6} Torr in the nozzle and utilization chamber, respectively. The primary beam intensity was about 10^{19} mole sr^{-1} sec^{-1}. The attenuation used was typically 10%. The secondary-beam gas flow could be interrupted by an electromagnetic valve and the gas could be sent at random into the scattering chamber through another inlet, keeping the background pressure in the utilization chamber constant. Typically 25% of the signal was present with no secondary flow, 25% came from the molecules scattered by the random flow, and the remaining 50% represented the molecules scattered by the target beam. The detector-signal amplification and in-

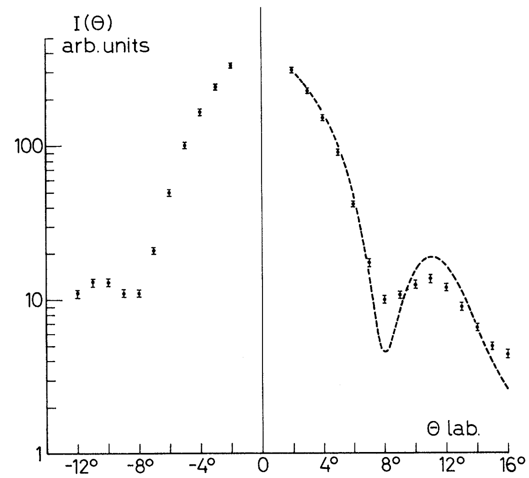

FIG. 2. Experimental points and computed predictions. Dashed line, Phillipson-Morse-Dalgarno (PMD) (r_m = 2.973 Å, other parameters as in Ref. 7).

tegration was performed by using standard lock-in techniques with integration times up to 3 sec. Full experimental details will be published elsewhere.

The experimental results are reported in Fig. 2. The points at the positive angles are the averaged results of several runs: The reproducibility from run to run was within a few percent. The experimental points at the negative angles show that the symmetry of the scattering is satisfactory. Also shown in Figs. 2 and 3 is the energy flow as a function of angle calculated by an "exact" numerical solution of the Schrödinger equation. The potentials and numerical values of the parameters used are given in the figure captions. These have been chosen among the commonly accepted interaction potentials for helium.[7,8] In the computations the finite angular and energy resolution of the apparatus has been taken into account. Theoretical and experimental points have been normalized at 2°.

The energy accomodation coefficient on the bolometer surface has been taken to be independent of the particle energy. This is justified because the maximum difference in energy between deviated and undeviated particles is of the order of 10%.

From Fig. 3 it can be seen that the positions of the extrema, which depend essentially on r_m, give for this parameter a value of 2.93 ± 0.05 Å in agreement with the value obtained in our laboratory from the measurement of the velocity dependence of the total collision cross section.[9] On the contrary the measured oscillation has an

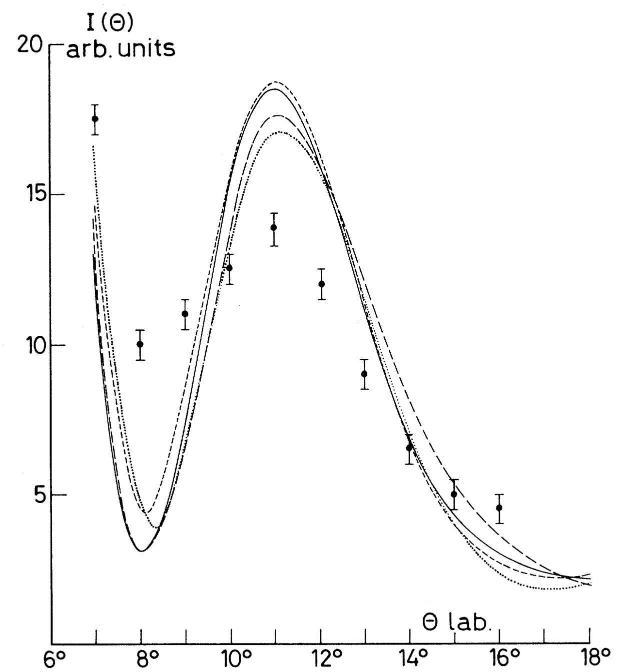

FIG. 3. Experimental points and computed predictions between 7° and 17°. Solid line, FMV potential (Frost-Musulim-V_{DD} potential with $\epsilon = 1.73 \times 10^{-15}$ erg, $r_m = 2.98$ Å, $c = 8.008\,77$, $r_2 = 3.510\,78$ Å, $C_6 = 1.41 \times 10^{-12}$ erg Å^6, $C_8 = 3.82 \times 10^{-12}$ erg Å^8). (See Ref. 8). Dotted line, Lennard-Jones 12-6 potential (with $\epsilon = 1.41 \times 10^{-15}$ erg, $r_m = 2.86$). Long-dashed line, Lennard-Jones 12-6 potential (with $\epsilon = 1.41 \times 10^{-15}$ erg, $r_m = 2.93$). Dashed line, PMD potential ($r_m = 2973$ Å; other parameters as in Ref. 7).

amplitude substantially smaller than predicted.

Unfortunately the discrepancy between experiment and theory is of the same kind as the discrepancy that should be found in an apparatus of insufficient resolution. On the other hand, to reproduce the experimental results with the given potentials, a quite unlikely low angular and energy resolution are to be ascribed to the apparatus. Furthermore the present results are consistent within 10% with previous measurements performed with an angular resolution worse by a factor of 2 and are not affected by different positioning of the thermal shields. Therefore to report our data at this stage will show that this kind of measurement is possible and may prove useful in general.

In conclusion, we can only say that at energies corresponding to room temperature all the potentials examined predict very similar results, which are in fair agreement with the experimental cross sections. To discriminate between different potentials, work should be done with different beam energies and we plan to do this along with work on other systems.

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[1]Ch. Schlier, Ann. Rev. Phys. Chem. 20, 191 (1969).

[2]R. B. Bernstein and J. T. Muckerman, Advan. Chem. Phys. 12, 389 (1967).

[3]R. W. Bickes and R. B. Bernstein, Chem. Phys. Letters 4, 111 (1969).

[4]D. H. Winicur, A. L. Moursund, W. R. Devereaux, L. R. Martin, and A. Kuppermann, J. Chem. Phys. 52, 3299 (1970).

[5]J. B. Anderson, R. P. Andres, and J. B. Fenn, Advan. Chem. Phys. 10, 275 (1966).

[6]M. Cavallini, G. Gallinaro, and G. Scoles, Z. Naturforsch. 22A, 413 (1967).

[7]R. B. Bernstein and F. A. Morse, J. Chem. Phys. 40, 917 (1964).

[8]L. W. Bruch and I. J. McGee, J. Chem. Phys. 46, 2959 (1967).

[9]M. G. Dondi, G. Scoles, F. Torello, and H. Pauly, J. Chem. Phys. 51, 392 (1969).