Velocity Dependence of the Total Cross Section for the Scattering of Li and K by Xe*

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The velocity dependence of the total cross section has been measured for the scattering of potassium by xenon at relative velocities between 350 and 1550 m/sec, and for the scattering of lithium-7 by xenon between 700 and 3800 m/sec. Although small deviations were seen, the potassium-xenon scattering was in general agreement with the Massey-Mohr theory, assuming an inverse sixth power interatomic potential. Large deviations from this theory were observed for the lithium-xenon scattering. To account for these deviations, phase shifts were calculated in the semiclassical framework of Ford and Wheeler, following a method of Bernstein. The Lennard-Jones interatomic potential was assumed. The velocity dependence of the cross sections which were calculated from the phase shifts shows the qualitative features of the experimental results.

INTRODUCTION

SCATTERING of neutral molecules at thermal velocities has been studied in a number of recent experimental investigations. Measured values of the total cross sections have been expected to yield information regarding the long-range van der Waals forces.[1–5] Massey and Mohr[6] have derived an approximate relation between the intermolecular-potential constant, C, the relative velocity, v_r, and the observed total cross section, Q. Their treatment requires the use of many partial waves which have large phase shifts, so that the values of the latter become essentially random after integral multiples of π are subtracted. For the long-range attractive potential $V(r)=-C/r^s$, the equation may be written in the alternative forms

$$Q=g(s)(C/v_r)^{2/(s-1)}=Q_0(s)v_r^{-2/(s-1)}, \qquad (1)$$

where $g(s)$ is a known function. Experiments have indicated that absolute values of Q predicted by Eq. (1) may be somewhat less than experimental values.[1,5]

Bernstein[7,8] has presented a calculation of the phase shifts, and of the total cross sections for the scattering of H_2 by Hg. He obtained a plot of $\log Q$ vs $\log v_r$ that did not give the straight line predicted by Eq. (1), but showed an undulatory character. These deviations were attributed to a nonrandom behavior of the phase shifts, which is caused by repulsive forces which were neglected in the derivation of Eq. (1).

Measurements of the total cross section as a function of velocity,[3,4] and of temperature,[2] appear to be in general agreement with Eq. (1) although Hostettler and Bernstein[9] obtained Li-Hg cross-section data, both total and differential, in which quantum effects were observed.

The velocity dependence of the total cross section for scattering of K and Li by Xe was measured in the present experiment. Atomic collisions were studied because rotational excitation in molecules appears to add further complications to interpretation.[10] Alkali beams were used because of experimental considerations. Xenon was chosen from the rare gases, because (a) it was expected to have the greatest attractive interaction and therefore the best agreement with the Massey-Mohr condition, and (b) it has a relatively slow speed which minimizes the spread of the relative velocity.

APPARATUS

The arrangement of the apparatus is shown in Fig. 1. It was divided into three separate chambers. Each contained a large liquid N_2 trap and was pumped by a 6-in. Hg diffusion pump. The apparatus was similar to that previously used for the scattering of beams which were not velocity selected.[1] The beam source was a stainless-steel oven of a two-chamber type similar to that described by Miller and Kusch.[11] The mechanical

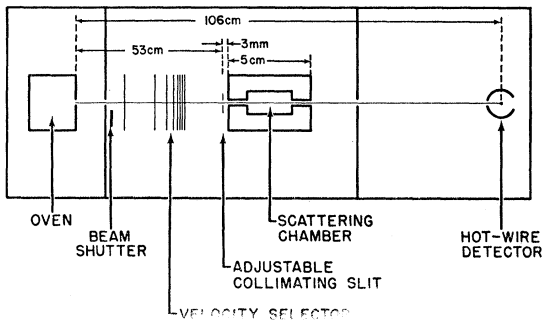

FIG. 1. Top view of apparatus (schematic). Drawing is not to scale.

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velocity selector, details of which have been presented elsewhere,[12] transmitted a beam with a velocity spread of about 3.4%. The dimensions of the scattering chamber were almost identical to the one previously used.[1] The chamber could be used at room temperature or at liquid N_2 temperature. The source slit was usually between 0.02 and 0.05 mm in width. The collimating slit width, which was adjustable, could be varied between 0.01 and 0.2 mm. A conventional surface ionization hot-wire detector was used. The wire, of 0.05-mm diam, was 92% Pt-8% W alloy obtained from the Sigmund Cohn Corp. The alloy was considerably less noisy than several available samples of "pure" W. For the measurement of the Li intensity the wire was continuously sprayed with oxygen. The scattering chamber and the collimating slit were fixed in position. The oven slit and the detector wire could be adjusted laterally and could be rotated in a plane perpendicular to the beam, so that both slits and the detector wire could be precisely aligned. The angular resolution of the apparatus, at the 50% level as calculated from the Kusch criterion (briefly described in reference 2), could be varied between 25 and 110 sec of arc.

The scattering gas pressure was measured with a Veeco RG75 ionization gauge tube which was operated at an emission current of 125 μA. The ion current at the detector was measured with a Cary model 31 vibrating reed electrometer with a $10^{11}\,\Omega$ input resistor. Typical ion currents (near the maximum of the velocity distribution curve) were about 3×10^{-12} A. Accurate cross-section measurements became difficult when the currents were less than about 10^{-13} A. The output signals from the ion gauge circuit, and from the Cary electrometer, were traced on a standard 2-pen, 10-mV strip-chart recorder.

MATERIALS

The K (B & A lump, Code 2080) was ~97.5% pure, the impurity being largely Na. Favorable vapor-pressure considerations, as well as the greatly reduced sensitivity of the detector to Na, served to reduce the effect of the impurity to negligible proportions. Li^7 obtained from Oak Ridge National Laboratory was used, and was stated to be chemically and isotopically >99% pure. Experimental tests showed no discernible impurities. The xenon (Air Reduction Co., research grade) was stated to have less than 0.1% impurity.

EXPERIMENTAL PROCEDURE

The slits and the detector wire were aligned with a telescope and then with the beam itself. When the slits were in position, the beam profile was measured by sweeping the detector across the beam. This profile was used to help estimate the angular resolution of the experiment. The detector was brought back to the center of the beam and the primary measurements were made. The beam velocity, c, was adjusted to a given value and the beam intensity, I, was then measured at 4 to 8 values of the scattering gas pressure which resulted in 20 to 70% attenuation of the beam. The zero line (shutter closed) and the 100% transmittance line, I_0, were obtained before and after each series of attenuations. The emission current in the ion gauge was held constant throughout the experiment. The beam velocity was then changed to another value and the process was repeated. Plots of $\log(I/I_0)$ vs the pressure of the scattering gas were linear. Mean free paths, λ_c, may be obtained from such plots by the relation $\lambda_c=-d/\ln(I/I_0)$, where d is the effective scattering chamber length. One set of data points was obtained with the scattering cell at 77.4°K, but all the rest were taken at room temperature. The normal operating pressure in the three vacuum chambers was about 2×10^{-7} mm Hg.

A knowledge of the angular speed of the velocity selector leads to correct values of the beam velocity only if the beam and selector axes are perfectly parallel, The nominal velocity at which a maximum beam intensity was obtained was always compared with that predicted from the temperature of the beam source. If, after realigning the beam, these velocities differed, the appropriate correction was made to the nominal selector velocities. Such corrections were less than 5%.

Pauly[3] has shown that for the interaction predicted by Eq. (1), a relationship may be obtained between the mean free path λ_c and the values of s. This is

$$\lambda_c=\frac{\pi^{1/2}c^{2/(s-1)}}{nQ_0F(s,x)}, \tag{2}$$

where F is a known function[3,13] and $x\equiv c/\alpha$. α is the most probable velocity of the scattering gas and n is its concentration. λ_c was computed from the data, at each velocity, for the same fixed value of n. A trial value of s was used to calculate F. Because the ion gauge was not calibrated, only relative values of n, and therefore of Q_0, were obtained. Consequently, d need not be determined; it is sufficient that it remains constant. Then if Eq. (1) is obeyed a plot of $\log(1/\lambda_cF)$ vs $\log c$ should give a straight line of slope $-2/(s-1)$. The total cross section Q, which can be compared with theory, was calculated by multiplying Q_0 by $v_r^{-2/(s-1)}$. Alternatively, one may compute Q from the equations of Schoonmaker,[4] which do not include a velocity dependence of the cross section in their derivation. Log$Q$ may then be plotted against $\log v_r$ and s may be determined from the slope. This method of finding s is not so rigorous as the Pauly plot. v_r was obtained from a relation quoted in Schoonmaker's[4] work.

Some experiments were performed to test the effect of the angular resolution upon the relative cross section.

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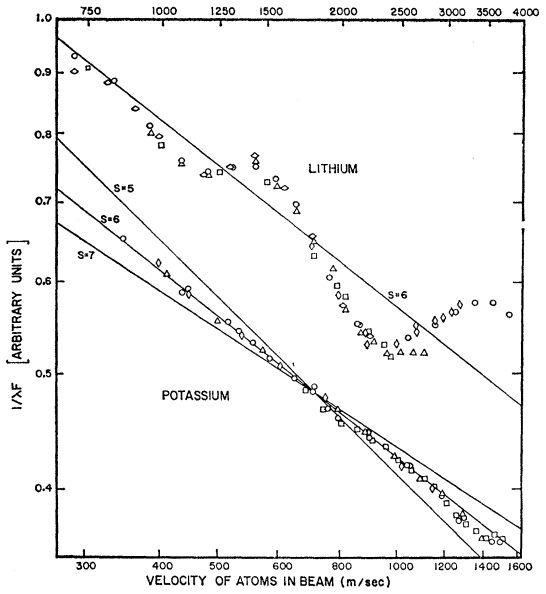

FIG. 2. Pauly-type plot showing experimental results compared to the predictions of the Massey-Mohr theory, assuming $s=5$, 6, and 7 for K-Xe and $s=6$ for Li-Xe. Different symbols represent data from different days. The ordinate is relative; the heights of the lithium and the potassium data should not be compared. The top and bottom abscissas refer to the lithium and potassium atom velocities, respectively.

Variations from 25 to 70 seconds of arc produced no change in the relative curve of Q vs v_r.

EXPERIMENTAL RESULTS

The results are shown in Figs. 2–4. A Pauly-type double log plot is shown in Fig. 2. The ordinate is relative; only the same symbol for the same interaction partners should be compared. On an absolute scale the K points would doubtless be above those of Li. For K, agreement with the Massey-Mohr line (at $s=6$) is fairly good, except for a small deviation at high velocities. With Li, much larger deviations were obtained. Although $F(6,x)$ was used in calculating all points, the results were little affected by the choice of s. For example, one set of K data (shown by the circles in Fig. 2) was calculated in four different ways: three using the Pauly method and one using the Schoonmaker approach. In the Pauly method, $F(5,x)$, $F(6,x)$, and $F(7,x)$ were evaluated. Least-squares slopes (of the variables of Fig. 2) were then obtained, and values of s were calculated from these slopes. These values were 5.80, 5.90, and 5.97, respectively. In the Schoonmaker method a least-squares slope of $\log Q$ vs $\log v_r$ led to $s=5.98$. In the Li case, because of the faster beam atoms, relative cross sections obtained from the four methods were virtually indistinguishable. Although Eq. (1) does not describe the data, this agreement indicates that the Pauly method may still be used to compute the cross sections. The relative cross sections were calculated from the best fit to the points in Fig. 2. These are plotted against v_r in Figs. 3 and 4. These experimental cross sections were normalized to theoretical values. The method of calculating these values is described in the next section. Because only relative cross sections were measured in this experiment, a better estimate of the absolute values may be obtained from a previous measurement[1] (without velocity selection) in which the cross sections for K-Xe at an average v_r of 650 m/sec was 1050 ± 150 Å^2.

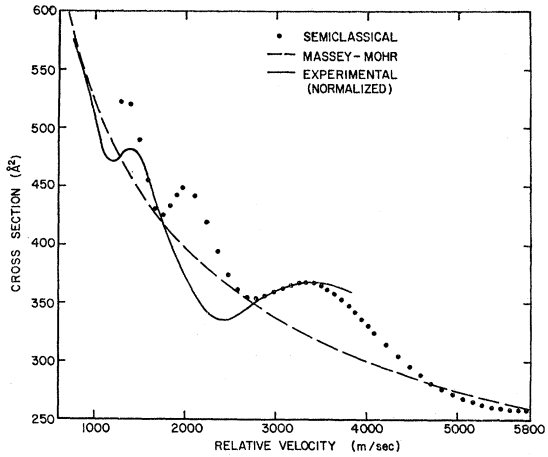

FIG. 3. Scattering of lithium-7 by xenon. The ordinate is correct for the theoretical values, but the experimental curve was normalized to the semiclassical prediction at 3400 m/sec.

CALCULATIONS OF THE CROSS SECTION

In an attempt to account for the scattering observations we computed the cross sections. Phase shifts, η, were calculated by a procedure outlined by Bernstein,[7,14] who used the semiclassical framework of Ford and Wheeler.[15] The two-parameter (ϵ,σ) Lennard-Jones interatomic potential,

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \qquad (3)$$

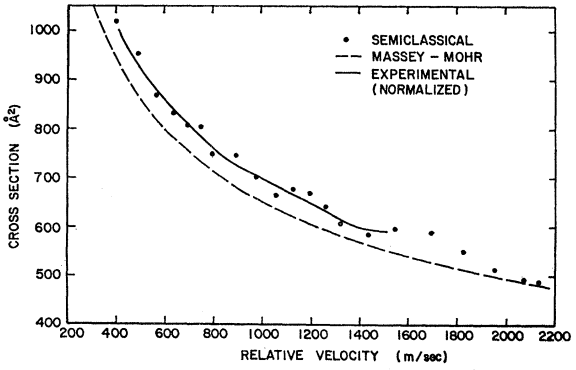

FIG. 4. Scattering of potassium by xenon. The ordinate is correct for the theoretical values, but the experimental curve was normalized to give a best fit to the semiclassical prediction between 500 and 1000 m/sec.

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was used for these calculations. The values used in the present case were $(\epsilon/k)_{\text{Li-Xe}}=446°\text{K}$, $\sigma_{\text{Li-Xe}}=3.46$ Å, $(\epsilon/k)_{\text{K-Xe}}=288°\text{K}$ and $\sigma_{\text{K-Xe}}=4.077$ Å. The Li-Xe parameters were obtained from a previous estimate of the Li-Hg parameters[9] by using tabulated parameters[16] for Hg and Xe and the usual combining laws.[16] The value $(\epsilon/k)_{\text{K-Xe}}$ was calculated from an experimental[17] $(\epsilon/k)_{\text{K-Hg}}$ and the σ from scattering data (using the ratio $C_{\text{Li-Ar}}/C_{\text{K-Ar}}$),[18,19] again using the combining laws.

Following Bernstein's notation we define the variables $k\equiv(2\mu E/\hbar^2)^{1/2}$; $A\equiv k\sigma$; $B\equiv 2\mu\epsilon\sigma^2/\hbar^2$; and $\beta'\equiv(l+\frac{1}{2})/A$ where μ is the reduced mass, E is the initial relative kinetic energy, and l is the angular momentum quantum number. Bernstein[7] has tabulated a reduced phase constant, η^* $(\equiv\eta/A)$, at given values of β', for several reduced kinetic energies, K $(\equiv E/\epsilon)$. η^*, when $K>0.8$, may be obtained from an integration of the classical deflection function.[14] This procedure is entirely equivalent to the JWKB method. We performed this integration and compiled tables of η^* vs β' similar to Table Va of reference 7 for values of K between 1 and 30. β' was tabulated from 0 to 2.5 at intervals of 0.1. For a given value of l, β' was calculated and the corresponding reduced phase constant was obtained by linear interpolation between the two nearest values of β'. For $\beta'>2.5$, phase shifts were evaluated by the Born approximation expression,[7] $\eta=(3\pi/8)A^4B/l^5$. The total cross sections were then computed from the phase shifts in the usual way. Many partial waves were required. For example, at the highest velocities calculated (i.e., at $K=30$) for Li-Xe and K-Xe, the cross section was at 99% of its final value after adding the contributions from 495 and 1145 partial waves, respectively. About 15 min of IBM-7090 computer time were required to calculate all cross sections shown in Fig. 3.

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS

Figures 3 and 4 show the predictions of the Massey-Mohr theory and those of the semiclassical approach. Also shown are the experimental cross sections normalized to the semiclassical prediction.

The main features are more pronounced for Li-Xe. The Massey-Mohr cross section decreases monotonically with v_r. The semiclassical curve shows undulations which are similar to the experimental result, although quantitative agreement was not obtained.

For K-Xe, the undulations in the semiclassical curve are much less pronounced. The composite experimental curve shows only slight signs of undulation, mostly at the higher velocities. Some of the individual sets of of data (see Fig. 2) appear to indicate greater deviations from the Massey-Mohr curve than the composite.

The K-Xe experiments were originally performed to find the best value of s from plots of the Pauly type (Fig. 2). For this purpose it is better to obtain data in a large range of velocities rather than in the small velocity region in which data on the deviations are best obtained.

Large errors may result from attempting to use this type of data to measure s. For example, Schoonmaker[4] used cross sections found at two velocities, computed s, and then repeated this process at other velocities. If this method is applied to the Li-Xe data (see Fig. 2), completely erroneous results may be obtained.

The semiclassical approach appears to represent a good basis for the interpretation of the results. Its failure to obtain quantitative agreement with experimental results may be due to a poor choice of parameters for the Lennard-Jones potential or to the need for a better potential function. *Note added in proof.* A much better fit to the data has been obtained using different values of ϵ and σ. This will be discussed in a paper now in preparation.

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