

Absolute measurements of total cross sections for electron scattering by Na₂ and K₂ (0.5–50 eV)*

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Absolute measurements have been made of total cross sections for the scattering of electrons by sodium and potassium diatomic molecules, over the electron energy range 0.5–50 eV, at temperatures of 405 and 335 °C, respectively, using the molecular beam recoil technique. We find the molecular cross sections to lie about 60% and 33% above the respective sodium and potassium atomic cross sections above 2 eV. The measured sodium and potassium molecular total cross sections range from 305 and 430 Å², respectively, at 0.5 eV and 85 and 97 Å², respectively, at 50 eV. The over-all uncertainty in the sodium dimer results is at most 16%, and in the potassium dimer results is at most 20%.

INTRODUCTION

A great deal is known about the structure of the alkali diatomic molecules; many photoionization,¹ spectroscopic,² and molecular beam resonance³ results have been reported. Much recent work has involved laser-induced fluorescence⁴ and laser-induced photolysis.⁵ In the latter, photodissociation of the alkali molecules Rb₂ and Cs₂ was found to be the initial step in an infrared alkali lasing process. Experimental and theoretical studies include both the homonuclear and heteronuclear alkali molecules. In a separate experiment in our laboratory the average static electric dipole polarizabilities of the homonuclear alkali dimers are being measured.⁶ We were motivated partly by these measurements to perform the present experiment, in which we have determined absolute total cross sections for electron scattering by the alkali dimers Na₂ and K₂, at temperatures of 405 and 335 °C, respectively.⁷

The alkali molecules are interesting as simple scattering targets because of their basic H₂-like character. The alkali dimers differ from H₂ in that they are loosely bound (~1 eV) with large internuclear spacings (~3–4 Å) and low ionization energies (~4–5 eV). At normal experimental temperatures the dimers are in their ground electronic and vibrational states, but a large number of rotational states are significant. The alkali dimers have been used as targets for scattering by hydrogen⁸ and chlorine⁹ atoms. Lee, Gordon, and Herschbach⁸ pointed out that because the alkali dimers are so loosely bound, they can play a role in chemical scattering analogous to that played by the deuteron in nuclear physics, and that one might expect to find examples of chemical reaction dynamics analogous to the two prototype modes found in deuteron scattering—direct reaction via a stripping process or resonance reaction

via compound nucleus formation. Related alkali atom-atom scattering experiments have also been performed.¹⁰

On the other hand, there have been no experimental or theoretical studies of electron scattering by the alkali molecules. Absolute total cross sections for electron scattering by the alkali atoms have been reported.^{11,12} The simplicity of alkali dimer beam production and detection, and the existence of detailed theoretical work¹³ on electron scattering by H₂ suggests an immediate extension of electron scattering studies to the alkali molecules.

II. METHOD AND APPARATUS

The apparatus used in these measurements has been described elsewhere, as it was set up for atomic alkali scattering work.¹² For the molecular cross section measurements, we have added a Stern–Gerlach magnet following the alkali oven (Fig. 1), to remove the atomic component of the beam. The Stern–Gerlach magnet was constructed to have a gradient-to-field ratio of 10 cm⁻¹ at the beam position. In Fig. 2 we show plots of the sodium beam intensity as the oven was scanned perpendicular to the beam axis, for different magnetic field strengths. The two atomic spin states are seen to be deflected by the magnet, leaving only a molecular beam on axis at sufficiently high field strengths. The molecular beam is cross fired by a magnetically collimated electron beam and downstream is surface ionized on a hot tungsten wire, mass analyzed, and detected with a continuous-channel electron multiplier. The electron gun design and performance has been discussed in detail separately.¹⁴ The electron beam is 0.08×2.51 cm² in cross section; the magnetic field is 1.1 kG.

We used the molecular beam recoil technique,

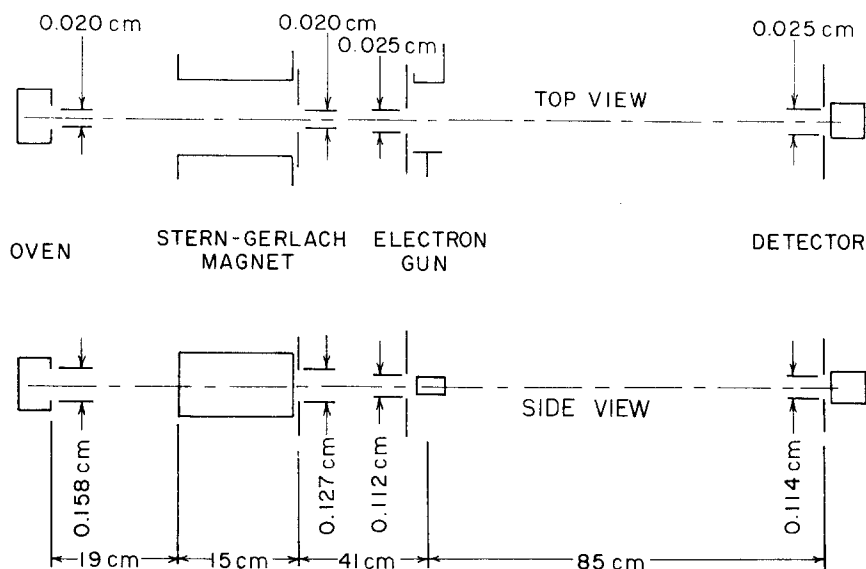


FIG. 1. A schematic diagram of the apparatus, giving relevant dimensions.

in which we observe the attenuation in the forward molecular beam intensity due to electron scattering. The particle multiplier output current was amplified by an electrometer, digitized, and accumulated by a multichannel scaler (MCS). Normally, the electron energy was held fixed as the electron current was cycled on and off, and after about one hour the MCS showed a statistically significant difference between the two integrated beam intensities obtained without and with scattering, respectively. This difference I_s is proportional to the scattered molecule intensity in the same way that the full count rate I_a is proportional to the full beam intensity. The measured total cross section is given in terms of experimental quantities by^{11,12}

$$\sigma_T = h \bar{v} I_s / I_a I_e, \quad (1)$$

where h is the atom beam height at the interaction region, \bar{v} is the average molecule speed in the beam source, I_s is the measured scattered molecule intensity, I_a is the full molecular beam intensity, and I_e is the electron particle current. Since I_s and I_a are measured with the same detection and counting system, any gain factors cancel (provided the system is linear). One principal advantage of the recoil technique is that the ratio I_s/I_a is the absolute fraction of molecules scattered, which leads to an absolute cross section without having to determine the actual magnitude of either I_s or I_a separately. The angular resolution error in the measurement of I_s/I_a will be discussed in Sec. IV. The factors h , \bar{v} , I_a , and I_e enter Eq. (1) from an evaluation of the electron and molecular beam overlap integral, which is simplified by assuming that the molecular beam is uniform over its height and by arranging slit

sizes so that all of the electrons pass through the molecular beam. Measurements of the oven temperature are used to obtain \bar{v} ; the oven temperature is such that the molecular flow from the oven is pure effusive.

In some cases we have set the MCS so that it

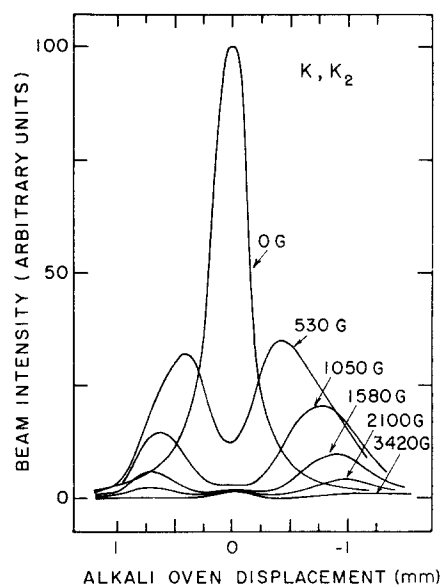


FIG. 2. Deflection of the atomic component of a sodium beam by the Stern-Gerlach magnet, leaving a sodium dimer beam in the forward direction. For this figure, the sodium oven was scanned perpendicular to the beam axis and the intensity at the detector was recorded, for various magnetic field strengths at the beam position. For molecular scattering, the highest field strength shown was used, in which case the beam is clearly non-atomic.

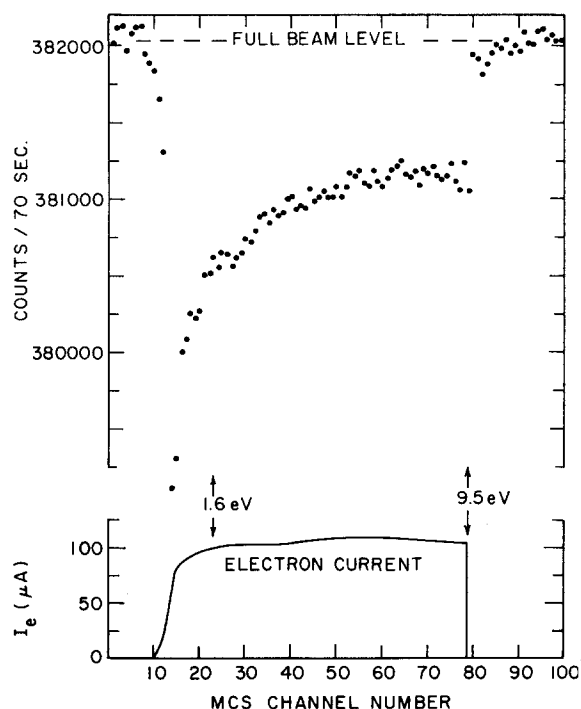


FIG. 3. Output of the multichannel analyzer, which is scanning the electron energy from 0 to 9.5 eV. The count rate is proportional to the integrated beam intensity in each channel during a 2 h run. Note the suppressed zero level. Attenuation of the beam due to electron scattering is indicated wherever the count rate is less than the full beam level (zero current). From channel-to-channel, both the electron energy and current are changing; the electron current is plotted below the beam data. The data below 1.6 eV were considered unreliable because the electron current density exceeded what we consider a safe level, at those energies, to avoid mutual repulsion problems. The scan rate is 50 msec per point, and the figure shows the integrated results of about 1400 scans.

scans the electron energy in small steps as it records the beam intensity,¹⁵ with small portions of the memory before and after the energy scan accumulating the full beam intensity (electron gun off). This technique was used for electron-potassium dimer scattering over the electron energy range 1.6–9.5 eV and 10.5–47 eV, with a scan rate of 50 msec/channel. The raw data from the MCS for the former case is shown in Fig. 3, the integrated results of about 1400 scans. The scattered molecule intensity at any particular electron energy is proportional to the difference in the full beam intensity and the attenuated beam intensity in the MCS channel corresponding to the electron energy of interest. This difference changes from channel-to-channel because the electron energy is increasing (the cross section is changing), and also because the electron current changes with energy, and because of statistical fluctuations. When this method is used, Eq. (1) is evaluated channel-by-channel and yields a detailed description of the total cross section as a function of energy. We consider the fixed-energy data more accurate, however.

III. DISCUSSION OF RESULTS

Our results for total electron scattering cross sections for the potassium and sodium dimers are shown in Figs. 4 and 5, and the fixed-energy data are tabulated in Table I. In the figures we have compared our molecular data to our atomic total cross sections.¹² We are not aware of any previous experimental or theoretical results for the dimers. For potassium, we find that the molecular cross section above 2 eV is 30–35% higher than the atomic cross section, even for energies

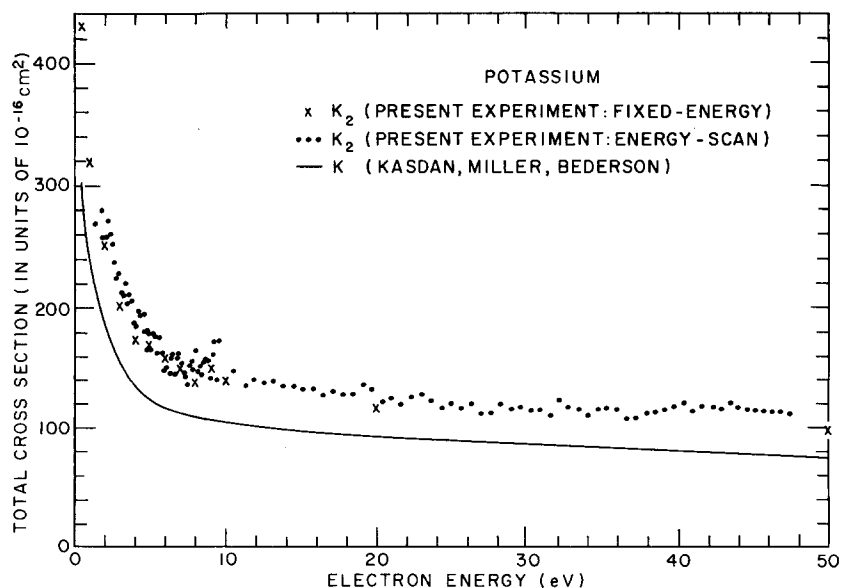


FIG. 4. Absolute total cross sections for the scattering of potassium diatomic molecules by electrons. The x marks are our fixed-energy data, and the points are our energy-scan data. We consider the fixed-energy points to be more accurate. The solid curve is the atomic potassium total cross section of Kasdan, Miller, and Bederson (Ref. 12).

TABLE I. A tabulation of our absolute total cross sections for electron scattering by sodium and potassium dimers, for the fixed-energy points listed. The uncertainty in the sodium data is 16% below 4 eV, and 14% above 4 eV. The uncertainty in the potassium data is 20% below 4 eV, and 15% above 4 eV.

Electron energy (eV)	$\sigma_T(\text{Na}_2)$ (\AA^2)	$\sigma_T(\text{K}_2)$ (\AA^2)
0.5	305	430
1	242	318
2	195	251
3	175	202
4	169	174
5	145	169
6	150	158
7	127	149
8	135	138
9	109	149
10	120	140
20	100	117
50	85	97

as large as 50 eV; below 2 eV the molecular cross section increases more rapidly than does the atomic cross section. The average value of the static electric dipole polarizability of the potassium molecule (with a rotational state distribution corresponding to 295 °C) is 40% larger than the scalar polarizability of the potassium atom.⁶ The most probable rotational quantum number at 335 °C is $J_m = 61$.

Although the shapes of the cross section curves versus electron energy for both the atomic and

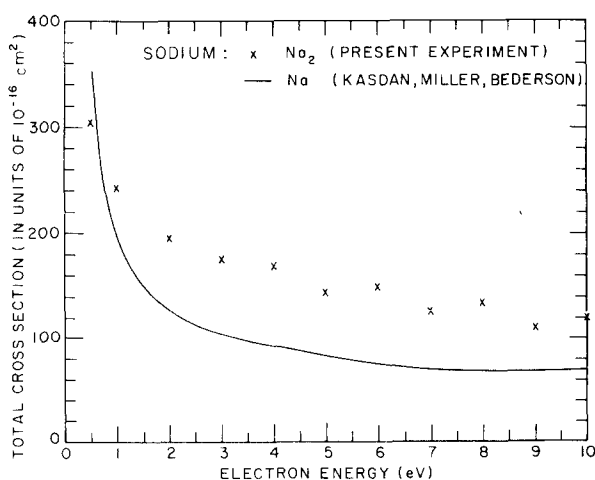


FIG. 5. Absolute total cross sections for the scattering of sodium diatomic molecules by electrons. The solid curve is the atomic sodium total cross section of Kasdan, Miller, and Bederson (Ref. 12). Not shown are our data for 20 and 50 eV: 100 and 85 \AA^2 , respectively. (The corresponding atomic sodium total cross sections are 65 and 57 \AA^2 , respectively.)

molecular species are certainly characteristic of scattering by highly polarizable systems, and the $-\alpha e^2/2r^4$ potential is clearly dominant, it is not possible to relate exactly the molecular and atomic cross sections solely through their average polarizabilities. The role of rotational transitions in the molecular scattering at low energies is significant,¹⁸ especially if the polarizability anisotropy is large. (A measurement of this quantity for the alkali dimers would be helpful; the anisotropy may be large because of the large internuclear spacing in the dimers. A calculation for Li_2 has predicted that the ratio of the average polarizability to the anisotropy is 2.9 for that molecule.¹⁷)

For sodium, as shown in Fig. 5, we find that the molecular cross section is 50–70% larger than the atomic cross section above 2 eV, even out to 50 eV, while below 1 eV the molecular cross section does not seem to be much different from the atomic cross section (down to 0.5 eV). However, the energy spread in the electron beam (250–300 meV) introduces some uncertainty even in a relative sense, at such low energies. The average value of the static electric dipole polarizability of the sodium molecule (with a rotational state distribution corresponding to 400 °C) is 60% larger than the scalar polarizability of the sodium atom.⁶ The most probable rotational quantum

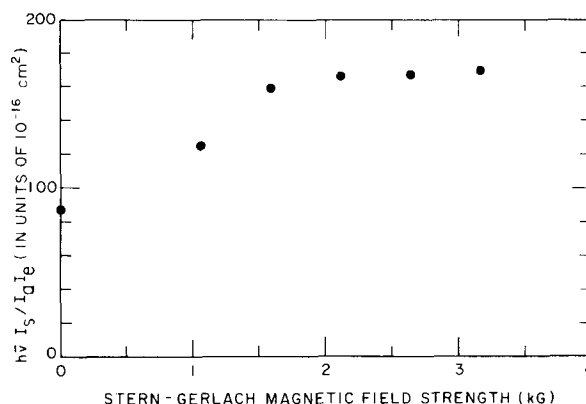


FIG. 6. A consistency check on the effect of the Stern-Gerlach magnetic field strength on the potassium data, at 5 eV. The points are evaluations of Eq. (1) with the presumption that the potassium beam particles have the molecular velocity distribution, for scattering signals obtained for various applied magnetic field strengths. At zero field strength, the beam density is over 99% atomic, while at high field strengths the atomic component has been removed. The largest field strength shown was used for all of the molecular cross section data in Figs. 4 and 5. The zero-field point yields the atomic potassium total cross section at 5 eV as measured by Kasdan, Miller, and Bederson (Ref. 12) provided a mass correction factor of $\sqrt{2}$ is applied.

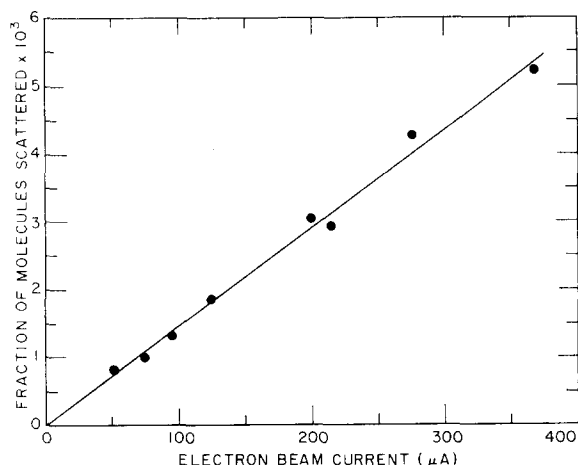


FIG. 7. Measurements of the fraction of sodium molecules scattered at 5 eV for various electron current values. The solid line is linear, as one would expect if the scattered fraction was proportional to the number of electrons used.

number at our operating temperature of 405 °C is $J_m = 39$.

IV. ANALYSIS OF EXPERIMENTAL UNCERTAINTIES

The beam particles are clearly the alkali dimers. The beam passes undeflected through a Stern-Gerlach magnet, is detected by surface ionization, and the ions are mass analyzed. In a similar apparatus in our laboratory, using the same alkali supply for measurements of static electric dipole polarizabilities of the alkali dimers,⁶ time-of-flight measurements have been made to check the velocity distribution of the dimers.

Figure 6 shows a measurement of an apparent total cross section for electron scattering of potassium beam particles at 5 eV as the magnetic field strength in the Stern-Gerlach magnet was increased. At zero field, the beam density is over 99% atomic, and the transition to a pure molecular beam can easily be seen as the magnetic field is increased. (The values of the apparent total cross section given are evaluations of Eq. (1) using the *molecular* velocity, hence the value at zero field strength differs from our atomic cross section¹² at 5 eV, as given in Fig. 4, but can be converted to the correct atomic value with a mass correction factor of $\sqrt{2}$.)

We have made experimental consistency checks with the apparatus for the sodium and potassium dimers. In Fig. 7 we show an example of measurements of the scattering signal for different electron beam currents for electron-sodium molecule scattering at 5 eV. The fraction of molecules scattered is seen to increase linearly with

the number of electrons used.

Possible errors associated with this electron gun have been discussed earlier.^{11,12,14} The presence of secondary or reflected electrons is most easily determined by moving the detector off axis in directions both parallel and antiparallel to the direction of the electron beam. Recoil-scattered molecules should only be seen on the parallel side; this is the case in our present experiment. The electron gun anode was biased to suppress secondary electrons. The electron energy is measured by a retarding potential technique using a small sample of the full electron beam. The result is consistent with atomic recoil angles measured in a separate experiment on this apparatus,^{11,12} and our electron energies should be considered uncertain by 0.15 eV. The electron currents used were always low enough to avoid space charge depression of the electron energy: from a maximum of 50 μA at 0.5 eV to 300 μA for energies above 10 eV. The electron current measurement is assigned an uncertainty of 1%.

In Fig. 8 we show an example of measurements of the total cross section for different oven temperatures, for electron-sodium molecule scattering at 5 eV. The apparent cross section is seen to be independent of the oven temperature within the statistical uncertainty. The range of temperatures is such that the beam intensity changes by a factor of 15, the average beam velocity changes by about 8%, and the most probable rotational quantum number changes by 3 (out of 39).

The molecular beam height h at the interaction region is determined by a slit in front of the elec-

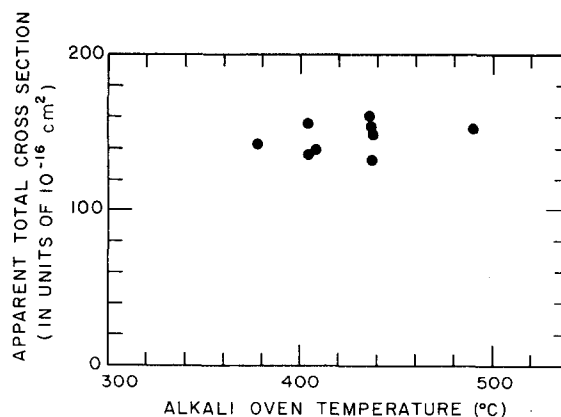


FIG. 8. A consistency check on the effect of the molecular beam intensity and temperature for electron-sodium dimer scattering at 5 eV. The range of temperatures is such that the beam intensity changes by a factor of 15, the average velocity by about 8%, and the most probable rotational quantum number changes by 3 (out of 39).

TABLE II. Results of an angular resolution calculation for our apparatus. The angles given are the electron polar scattering angle at which our detection efficiency is 0.5. For smaller angles the detection efficiency worsens, and for larger angles it increases to unity. The corresponding errors in the molecular total cross section were estimated from angular detection efficiencies, and scaled-up atomic differential cross sections of Karule (Ref. 18). The error always results in a measured cross section which is less than the correct cross section.

Molecule	At 0.5 eV	At 1 eV	At 5 eV
Na ₂			
Angular resolution	10°	7.5°	4°
Total cross section error	2.9%	2.8%	0.8%
K ₂			
Angular resolution	12°	9°	4.5°
Total cross section error	4.7%	6.3%	1.3%

tron gun, 0.112 cm high, and we assign an uncertainty of 1% to this quantity, which directly enters the cross section expression, Eq. (1).

The average molecular speed \bar{v} in Eq. (1) is determined from the alkali oven temperature as measured with a thermocouple imbedded in the oven block near the exit slit. The oven vapor pressure is low enough (~ 0.4 torr) to assure free molecular flow from the oven. Although we have no independent method for checking the molecular beam speed with this apparatus, atomic beam speeds have been checked with this apparatus by measuring the recoil angles of inelastically scattered atoms.^{11,12} Furthermore, time-of-flight measurements in a similar apparatus in our laboratory have been made for the dimers. We consider the molecular speeds uncertain by at most 5%.

The angular resolution error of the apparatus has been calculated using an analysis of the experiment detailed in Ref. 12, and representative values are given in Table II. The finite resolution of the recoil experiment results from scattering through angles which are too small to cause scattering out of the forward beam, thereby not contributing to the measured total cross section. The error in the total cross section caused by this finite resolution can be calculated only if the differential cross section is known. Since we are not aware of any other experimental or theoretical electron scattering results for the alkali dimers, we have simply scaled up the atomic differential cross sections of Karule.¹⁸ (In fact, the calculation of the angular resolution error requires only knowledge of the shape of the differential cross section curve versus angle.) This procedure is hardly exact but should suffice for the error esti-

mate needed here. The error always results in a measured value which is less than the correct cross section. Our calculations indicate an angular resolution error in the sodium dimer data of about 3% below 4 eV, and 1% above 4 eV. For the potassium dimer results, the angular resolution error is as much as 7% below 4 eV, and 2% above 4 eV.

The statistical uncertainty in the fixed-energy data is at worst 6%. A total of 22 fixed-energy data were obtained for the potassium molecule, along with a detailed scan of the electron energy range 1.6–47 eV. A total of 25 fixed-energy data were obtained for the sodium molecule. The combined statistical and systematic uncertainty for the sodium results, without regard to sign, is a maximum of 16% below 4 eV, and 14% above 4 eV. For the potassium results the over-all uncertainty is a maximum of 20% below 4 eV, and 15% above 4 eV. In addition, in examining our results one should consider our electron energies uncertain by 0.15 eV, and at very low energies our electron energy spread of 250 meV full-width at half-maximum is important.

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