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van der Waals forces between a Cs atom or a CsCl molecule and metal or dielectric surfaces

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The interaction protentials between a spherically symmetric atom (Cs) and a highly conducting surface (gold) or a dielectric surface (glass) are investigated by the atomic-beam-deflection technique. The observed beam profile is least-squares fitted to an r^{-3} potential. The derived interaction constant for the gold surface is 0.59 and 0.67 of the values predicted by Bardeen and Mavroyannis, respectively. A glass surface is found to have an interaction constant 0.65 that of gold. The measurements have also been obtained for a polar molecule (CsCl). With a gold surface the observed beam profile is almost identical to that for stainless steel (reported earlier) in spite of their difference in dc conductivity. Further, the observed constant for an insulator (glass surface) is 0.86 that of gold. With gold, the interaction constant obtained for a cesium-halide molecule, with a strong permanent dipole moment, is smaller than that for a Cs atom with zero dipole moment.

INTRODUCTION

The molecular-beam-deflection technique has been used to investigate the interaction between a polar molecule and a conducting surface by Shih, Raskin, and Kusch[1] (hereafter SRK). It was found that this interaction can be described by a dipole interacting with its image. On the other hand, in view of physisorption phenomena, there is no doubt that an attractive force with a surface still exists even for atoms with, of course, no permanent electric dipole moment. We wish to investigate the interaction potential between an atom and a surface, and to determine if the form and strength of this potential differs significantly from that of a molecule with a permanent dipole moment.

The interaction potential between an atom and a conducting surface has been a subject of theoretical work for many years, and a potential of the form

$$V = -K/R^3 \tag{1}$$

has been proposed by Lennard-Jones,[2] Bardeen,[3] and Mavroyannis[4] where K is the interaction constant, and R is the separation between the atom and the surface. Lennard-Jones took the surface to be an ideal conductor, deriving an interaction constant of

$$K_{\text{L-J}} = \tfrac{1}{12} e^2 \langle r^2 \rangle_{\text{av}} , \tag{2}$$

where $\langle r^2 \rangle$ is the mean-square displacement of all the electrons in the atom, and e the electronic charge.

Bardeen and Mavroyannis attempted to evaluate the correction arising from the finite resistivity of the conductor. The interaction constant obtained by Bardeen is

$$K_{\text{B}} = K_{\text{L-J}} \frac{Ce^2/2r_s\Delta}{1 + Ce^2/2r_s\Delta} , \tag{3}$$

where C is 2.6 for monovalent metal, r_s is the radius of a sphere whose volume is equal to that occupied by a conducting electron, and Δ is the ionization potential of the atom.

The interaction constant obtained by Mavroyannis is

$$K_{\text{M}} = K_{\text{L-J}} \frac{\hbar\omega_p/\sqrt{2}}{\Delta + \hbar\omega_p/\sqrt{2}} , \tag{4}$$

where ω_p is the plasma frequency of the metal.

The above theories can be extended to molecules as, for example, in the expression for diatomic molecules presented by SRK.[1] However, we are unable to evaluate the interaction constants expressed by Eqs. (2)–(4), since the wave function of the molecule used in this experiment is not known.

In the work of SRK, a small deviation from the R^{-3} potential form was observed for conducting surfaces made of either stainless steel or electroless nickel. One of the purposes of this work is to determine if the observed deviation is a consequence of the characteristics of the conducting surface. We will present here data involving surfaces made of pure metal (gold surface) or dielectric material (glass surfaces). We have chosen gold because it is a simple metal, chemically inert, and nonmagnetic. The last property is important when the deflecting atomic species, such as Cs, possesses an orbital magnetic moment.

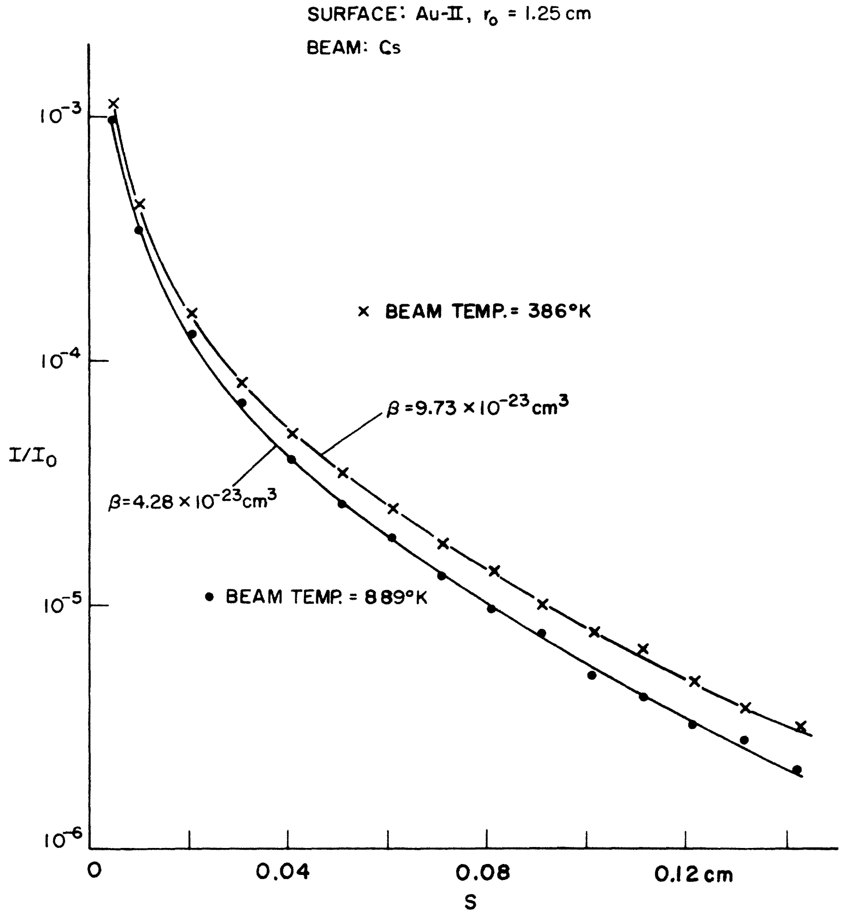

FIG. 1. Beam profiles of Cs beams deflected by a gold surface are shown together with respective least-squares-adjusted theoretical profiles. The dependence of a beam profile on the evaporation temperature is clearly demonstrated here.

EXPERIMENTAL

The interaction potential under study is investigated through the study of the deflection of a beam of atoms or molecules by the surface. The deflected intensity $I(S)$ relative to the full beam intensity I_0 is measured as the function of distance S into the geometric shadow of the surface. This intensity distribution is referred to as the beam profile. For those atoms (or molecules) deflected into the angles of deflection observed in the experiment, that is between 0.1 and 2.8 mrad, the impact parameters of the molecules are typically between 800 and 350 Å.

The observed profile is to be compared to a family of profiles calculated on the basis of the inverse-cube potential predicted by the literatures cited. The comparison will determine whether or not the interaction can be described through an r^{-3} potential within experimental limitation. If it can, the comparison will further yield a value of the interaction constant.

The apparatus is housed inside an ultrahigh-vacuum system, and the measurements are taken with the pressure below 5×10^{-11} Torr. A detailed description of the experimental setup and the beam-profile calculation has been described in an earlier paper.[1]

Two gold surfaces and a glass surface have been used in this experiment, and they are cylinders of 1-in. diameter and 2-in. height. The two gold surfaces are films about 3000 Å thick and prepared by vacuum deposition on a glass surface and a stainless-steel surface. The gold surfaces are prepared in a vacuum of 10^{-7} Torr. Prior to the deposition, the substrates are cleaned chemically as well as by ion bombardment. A vertical evaporation method is used with the gold source placed 15 in. below the substrate, and constantly rotating at an angular velocity of 20 rpm. During the coating, the pressure rises to 2×10^{-5} Torr.

The thickness of the evaporated film is monitored by the frequency reading of a quartz-crystal oscillator which is placed near the substrate. A test piece is first coated, and the thickness of the coating is measured by a multiple-beam interferometer. Thus, the relation between the

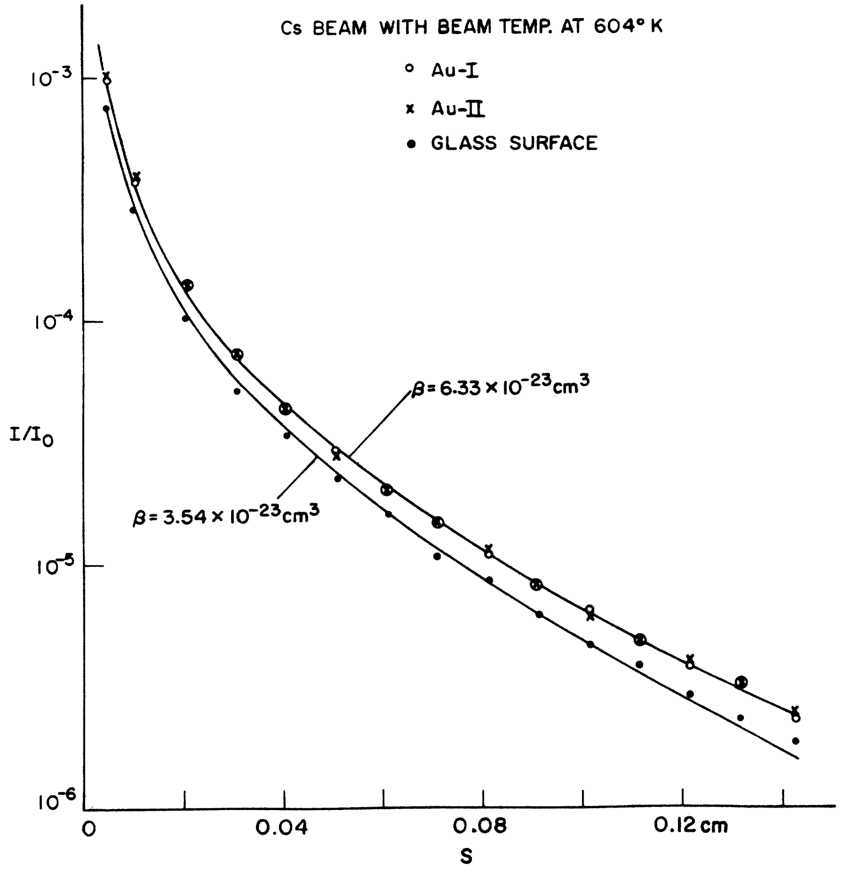

FIG. 2. Beam profiles of a Cs beam deflected by gold surfaces and a glass surface are shown with respective least-squares-adjusted theoretical profiles.

thickness of the coating, and the incremental frequency of the crystal oscillator is established. It takes 15.6 min to coat a gold film of about 3000 Å on each of our cylindrical substrates.

One of the substrates is the stainless-steel cylinder which has been used as a deflector in the previous experiment. This surface is polished to $\frac{1}{20}$ of the wavelength of green light (~250 Å). The other substrate as well as the glass surface is an ordinary drawn Pyrex glass tubing. According to Tolansky,[5] an ordinary drawn glass tubing can be extraordinarily smooth and has quite structure-free topographies under the examination of multiple-beam interferometry. We have neither measured the surface roughness of the glass surface, nor that of the Au-coated surfaces. Noncontacting methods which do not deform the surface under examination, are not yet available to measure the detailed topography of a cylindrical surface. Nor do we have a workable model to study the effect of the surface roughness, even if given the detailed information on the topography. Nevertheless, we do not believe the deflected-beam profile is affected by the surface roughness of such small magnitude as present on the surfaces. The substrates of the two gold surfaces are quite different in terms of the surface topographies, and yet the beam profiles of these two surfaces agree very well with each other. Even the difference between the profiles of the gold surfaces and the stainless-steel surface is very small.

The good agreement between the observed beam profiles of the two Au-coated surfaces indicates that the gold coating is thick enough to act as a a bulk metal as far as the interaction with atoms or molecules is concerned.

The beam profile which results from the interaction of a beam of atoms or molecules with a surface depends on the material and radius of the surface, as well as on the material and evaporation temperature of the beam. The dependence on all these parameters except the beam temperature has been demonstrated in the earlier experiment with molecular beams of cesium halides. The difficulty in varying the beam temperature lies in the fact that a significant change in the temperature results in such a large change in the beam intensity that either the full beam intensity is too large or the deflected intensity is too small

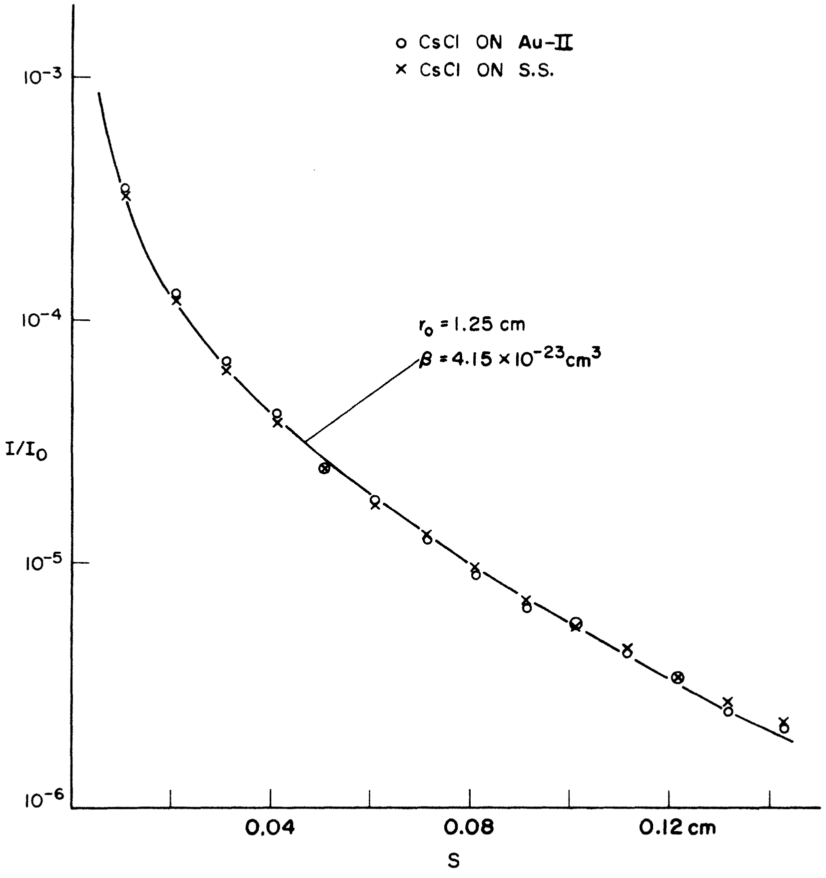

FIG. 3. Observed profiles of a CsCl beam deflected by a gold surface and a stainless-steel surface are shown together.

to be detected with the detection scheme employed. A Cs beam, however, can be produced by so-called reaction techniques as well as by the direct evaporation from Cs metal.

A method reported by Scheer and Fine[6] is to heat a mixture of 1:2 mole ratio of cesium chromate and powdered Si. Using this method, a Cs beam of a suitable intensity is produced, and the evaporation temperature is 889 °K. The conventional reaction technique[7] is to heat the mixture of powdered metallic calcium and CsCl. With this method, we produce a Cs beam at an evaporation temperature 604 °K.

The preparation of an oven charged with Cs metal is slightly complicated because of the high reactivity of Cs with air. Cs metal of 99.98% purity is first distilled under vacuum into a glass capsule, and this capsule is then sealed and placed in the cavity of a conventional oven.[8] After high vacuum is achieved in the chamber which houses the experimental apparatus, the capsule is broken with a push rod through an external control. In this way, we produce a beam of Cs at 386 °K.

With the Cs beams produced in the manner just described, the observed beam intensity at a given deflection is found to be lower for a beam with lower evaporation temperature. This qualitative feature is expected whatever is the form of the potential that governs the beam deflection. In particular, with the potential assumed to be $-K/r^3$, a calculated beam profile is characterized by a parameter $\beta = K/E$, where E is the kinetic energy of a particle in a monoenergetic beam. For a beam with Maxwellian velocity distribution, there is an effective kinetic energy $E_{\text{eff}} = 1.4kT$ where k is Boltzmann's constant and T the evaporation temperature. Thus, theoretically, $\beta = K/1.4kT$. While each observed profile indicates a small deviation from an r^{-3} potential, the least-squares-determined β is found to be consistent with the analysis based on this potential, that is $\beta \propto T^{-1}$.

RESULTS

The deflections of a Cs and CsCl beam by a gold surface and a glass surface have been measured and the result indicates a small but systematic deviation from an inverse-cube potential. The least-squares adjustment of the observed profile to a theoretical profile is made. The cal-

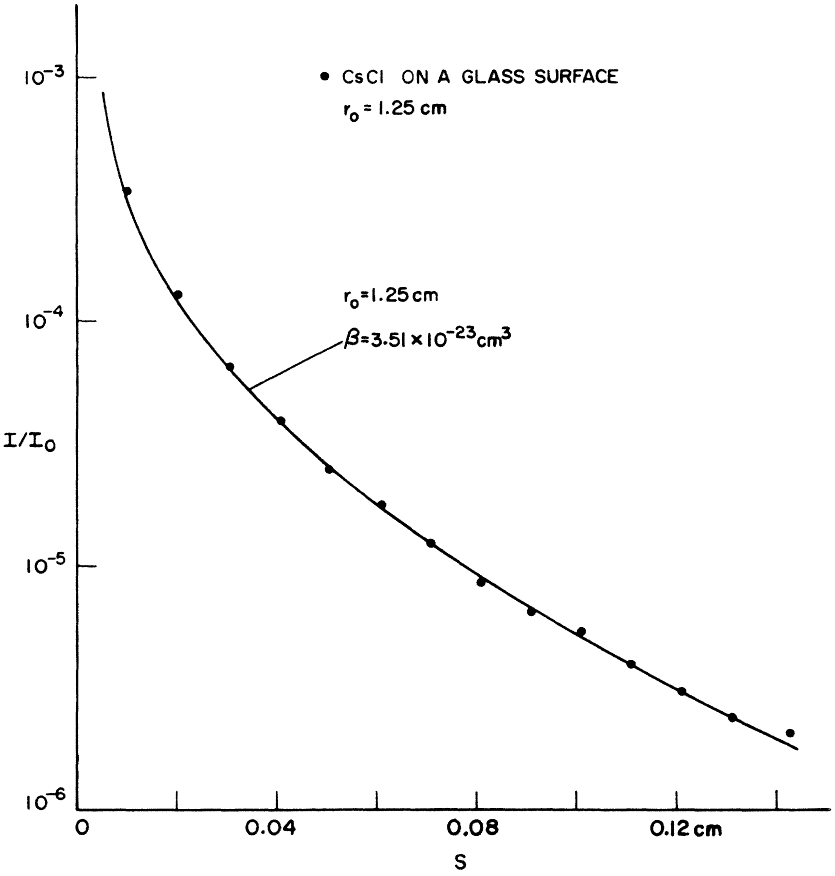

FIG. 4. Observed profile of a CsCl beam deflected by a glass surface is shown together with its least-squares-adjusted theoretical profile.

culation of a theoretical profile is discussed in an earlier paper.[1] The observed profiles are shown together with their respective least-squares-fitted theoretical profiles in Figs. 1–4.

The functional deviation is revealed by the fraction of deviation as a function of the deflection distance S, that is

$$f(S)=\frac{Y(S)-I(\beta,S)}{Y(S)}, \tag{5}$$

where $Y(S)$ is the observed intensity, and $I(\beta,S)$ the calculated value with least-squares-determined β. This function is shown in Figs. 5–7 for some of the cases. Common to all of the cases, this function is U shaped. In an earlier experiment[1] in which the deflection of a CsCl or a CsF beam by a stainless-steel surface or an electroless nickel surface was measured, the result also indicates a similar systematic deviation from the profile calculated based on an r^{-3} potential. However, the functional deviation with the present set of surfaces is smaller than observed in the previous experiment. No longer observed is the systematic increase in deviation with increasing deflection distance at relatively large deflections. When the small deviation is ignored, approximate values of β are derived through least-squares adjustment, and are summarized in Tables I and II.

Either with a Cs beam or a CsCl beam, no significant difference is observed between the profiles of two gold surfaces which differ in their substrates, the difference in the observed profiles are small and random. (In Fig. 2, the observed profiles of a Cs beam deflected by the two gold surfaces are shown together. The two sets of data are so close that on many deflection distances they coincide.) We will refer to the Au surface deposited on a stainless-steel cyclinder by Au-I, and that on a glass cylinder by Au-II.

The deflected intensity of a Cs beam by a glass surface is significantly lower than that by an Au surface (see Fig. 2). In fact, the least-squares-determined β for the glass surface is only 0.56 of that for the Au surface. However, with a CsCl beam, the observed profile of the glass surface is barely distinguishable from that of the Au surface, and the least-squares-determined β for the

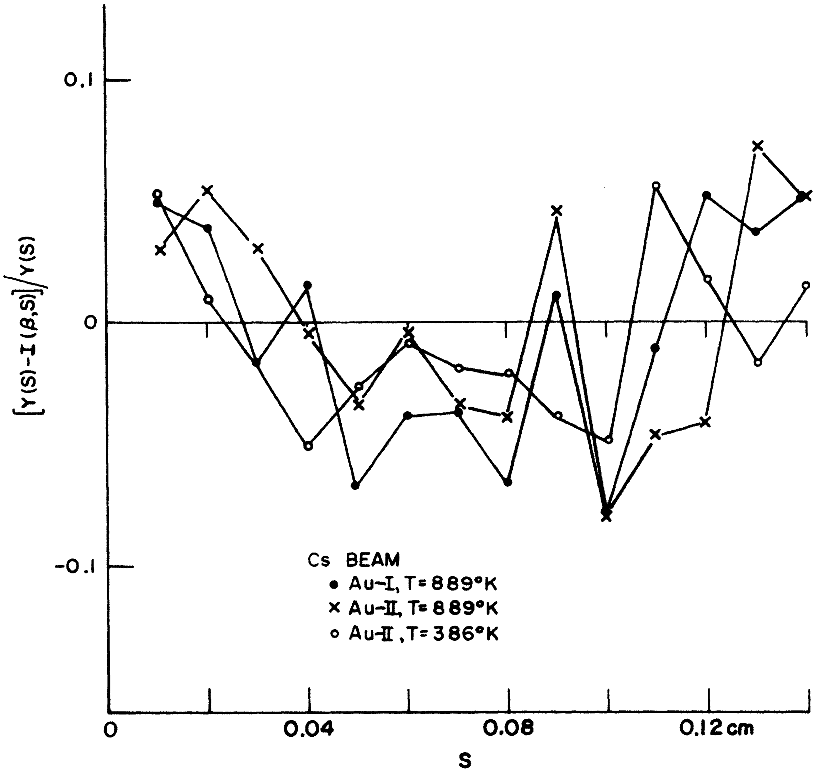

FIG. 5. Systematic deviation of an observed profile $Y(S)$ from a calculated profile $I(\beta,S)$ is demonstrated by the fractional deviation function plotted against the deflection distance S.

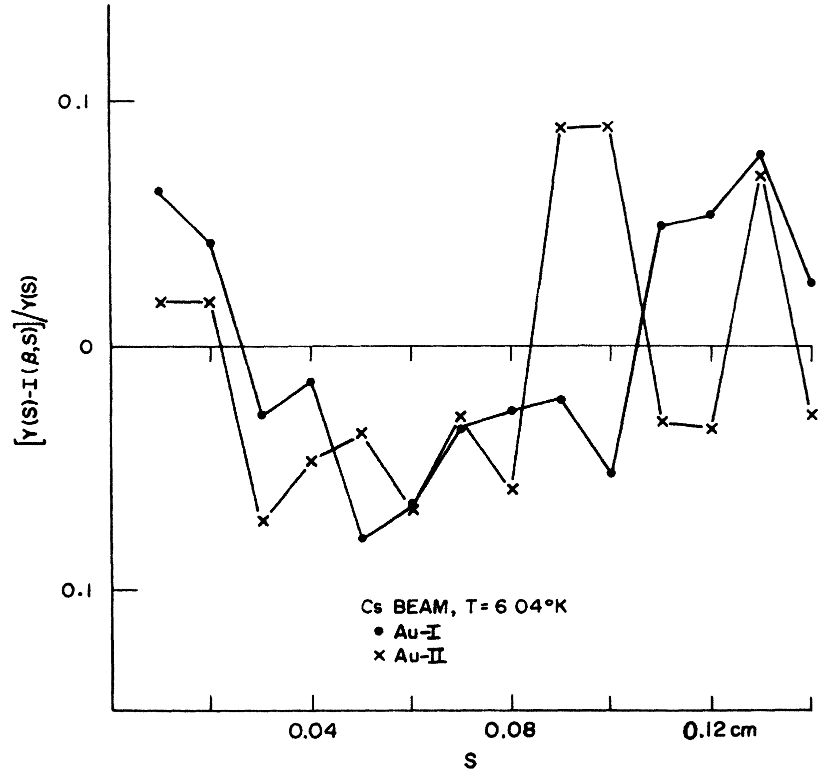

FIG. 6. Fractional deviations are shown for the cases of a Cs beam with $T = 604$ °K and deflected by gold surfaces.

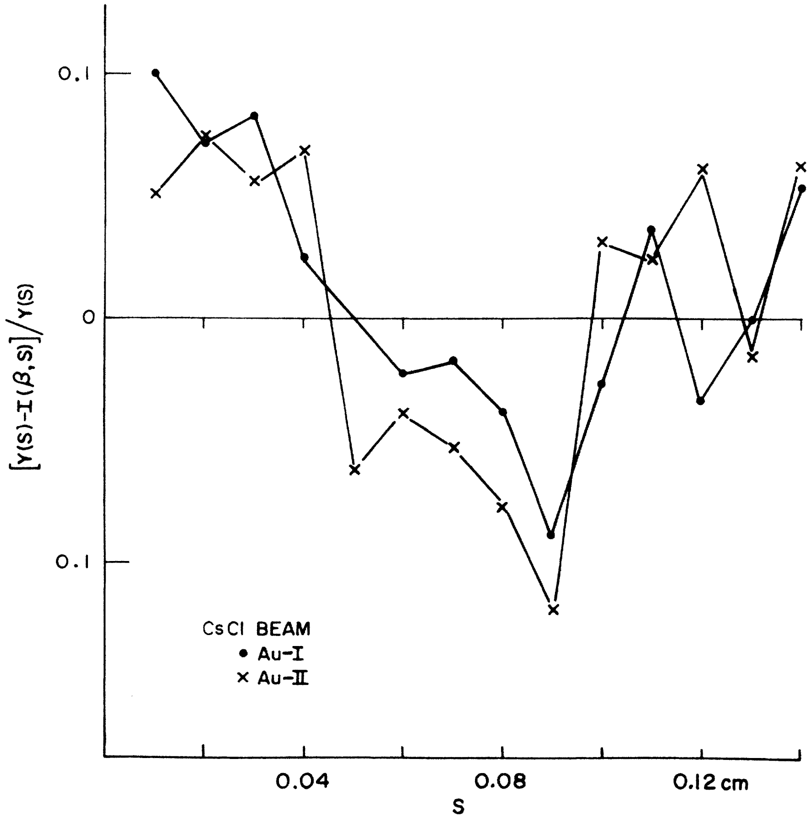

FIG. 7. Fractional deviations are shown for the cases of a CsCl beam deflected by gold surfaces.

glass surface is 0.86 of that for the Au surface.

In Fig. 3, the beam profile of a CsCl beam deflected by a gold surface is compared with the beam profile of a stainless-steel surface which is measured in the earlier experiment, and the difference is small. In fact, the least-squares-determined values of β shows trivial difference ($\beta = 4.15 \times 10^{-23}$ cm^3 for a Au surface and 3.94×10^{-23} cm^3 for a stainless-steel surface), even though Au with a resistivity 2.44 $\mu\Omega$ cm is a better conductor than the stainless steel with a resistivity 60 $\mu\Omega$ cm.

We have produced Cs beams with evaporation temperatures 889, 604, and 386 °K, and their full beam intensities are essentially the same. The deflected intensities are observed to increase with decreasing temperature (see Fig. 1). In spite of the small deviation of the observed profiles from an inverse-cube potential, our observation is consistent with the analysis based on an assumed r^{-3} potential; the least-squares-determined β is inversely proportional to T, the evaporation temperature. The observed interaction constant for Cs with a Au surface is 7.3 D^2 independent of the evaporation temperature, where D is the debye unit.

This observed interaction constant for Cs is smaller than the values predicted by Lennard-Jones, Bardeen, and Mavroyannis. The Lennard-Jones interaction constant can be evaluated by an approximation[9]:

$$K_{\text{L-J}} = \tfrac{1}{8}\alpha(E_1 - E_0), \tag{6}$$

where α is the static polarizability of the atom,

TABLE I. Experimental values of the interaction constant K for a Cs atom. β is the least-squares-determined value. K is calculated from β by the relation $K = 1.4kT\beta$ and expressed in debye units, where 1 D $= 10^{-18}$ esu.

	$T = 889$ °K		$T = 604$ °K		$T = 386$ °K	$T = 604$ °K
	Au-I	Au-II	Au-I	Au-II	Au-II	Glass
β(cm^3)	$4.28 \times 10^{-23} \pm 3\%$	$4.28 \times 10^{-23} \pm 3\%$	$6.33 \times 10^{-23} \pm 3\%$	$6.08 \times 10^{-23} \pm 5\%$	$9.73 \times 10^{-23} \pm 3\%$	$3.54 \times 10^{-23} \pm 3\%$
K(D^2)	$7.33 \pm 3\%$	$7.33 \pm 3\%$	$7.39 \pm 3\%$	$7.09 \pm 3\%$	$7.26 \pm 3\%$	$4.13 \pm 3\%$

TABLE II. Experimental values of the interaction constant K for a CsCl molecule.

	$T = 842\,^\circ\mathrm{K}$		
	Au-I	Au-II	Glass
$\beta\,(\mathrm{cm}^3)$	$3.96\times10^{-23}\pm4\%$	$4.15\times10^{-23}\pm5\%$	$3.50\times10^{-23}\pm5\%$
$K\,(\mathrm{D}^2)$	$6.44\pm4\%$	$6.75\pm5\%$	$5.69\pm5\%$

E_1 is the energy of the first excited state, and E_0 is the ground-state energy. For Cs, $\alpha = 63.3$ Å^3,[10] and $E_1 - E_0 = 1.39$ eV.[11] We then find $K_{\text{L-J}} = 17.6$ D^2. This value is the upper limit on the strength of the interaction, since the surface is considered to be an ideal conductor.

The values of the interaction constants calculated from the formulas of Bardeen and Mavroyannis are $K_B = 12.4$ D^2 and $K_M = 10.9$ D^2, respectively. In evaluating Eqs. (3) and (4), we have used the ionization potential $\Delta = 3.90$ eV[11] for Cs, and the plasma frequency ($\hbar\omega_p = 9$ eV) for gold,[12] and we calculated a value of $r_s \approx 2$ Å from the plasma frequency. The observed interaction constant 7.3 D^2 is 0.59 and 0.67 of the values predicted by Bardeen and Mavroyannis, respectively.

The interaction constant for a molecule is equal to the Lennard-Jones interaction constant $K_{\text{L-J}}$ multiplied by a correction factor due to the finite resistivity of the surface. This correction for a CsCl molecule and a gold surface is calculated to be 0.62 using Eq. (3) due to Bardeen and 0.53 using Eq. (4) due to Mavroyannis. (In these calculations, we have used $\Delta = 5.71$ eV which is the maximum in the absorption continuum of a CsCl spectrum.[13]) The Lennard-Jones constant includes the energy arising from both the permanent and the instantaneous dipole moments of the molecule.[1] Ignoring the contribution to the Lennard-Jones constant by the instantaneous dipole fluctuations since we are not able to determine it, the interaction constant for a CsCl molecule with a gold surface is evaluated to be 5.6 and 4.9 D^2 using the Bardeen and Mavroyannis correction factors, respectively. These calculated interaction constants are smaller than the observed value, 6.6 D^2. Thus the contribution due to the permanent dipole does not account for all of the interaction, but rather the major part of the interaction.

The experiments also reveal that the interaction potential of Cs is larger than that of CsCl although Cs, being an atom, has no permanent dipole moment. A plausible explanation for this phenomenon is that the portion of the interaction potential contributed by the instantaneous moment is small for a CsCl molecule but large for a Cs atom. Since the instantaneous moment is related to the polarizability [see Eq. (6)] and the polarizability of a Cs atom [$\alpha(\mathrm{Cs}) = 63.3$ Å^3] is much larger than that of a Cs$^+$ and Cl$^-$ ions (which are 2.44 and 3.69 Å^3,[14] respectively), the contribution due to the instantaneous moment in a Cs atom is larger than in CsCl and consequently the interaction in Cs is larger.

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