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# Alkali-Alkali Differential Spin-Exchange Scattering. II

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We analyze the data on differential spin-exchange scattering in collisions between alkali atoms which was presented in Paper I by Pritchard, Carter, Chu, and Kleppner. The data on the probability of exchange is analyzed to obtain the relative phase shift produced by the triplet and singlet potentials. A semiclassical impact approximation is developed and used to calculate this phase shift from theoretical calculations of the asymptotic behavior of the potentials. The results are consistent with the data only when the largest calculated value for the van der Waals potential is combined with the smallest calculated value of the difference potential. We have also analyzed the rainbow structure in the spin-summed differential cross section to obtain information about the depth and shape of the minimum in the triplet potentials in various alkali-alkali systems. Finally, we compare the result of our analysis with results from other experiments on alkali-alkali systems.

## I. INTRODUCTION

Measurements of differential cross sections for elastic scattering of alkali atoms by other alkalis, both with and without electron spin exchange, have been presented in the preceding paper[1] (called I hereafter). In this paper, we begin to analyze those data to extract the interatomic potentials for the alkali-alkali systems studied in I. This is a difficult task, since it is generally impossible to invert scattering cross sections to obtain potentials when quantum effects are important, even in elastic scattering where only one potential is involved. What we attempt here, then, is to find ways in which characteristic features of the potentials may be related to the scattering cross sections or to the angular dependence of the probability of spin exchange. We do this both by examining models which apply to exchange processes in general (spin exchange is similar to charge exchange,[2] which has been studied more extensively), and by showing how the well-developed techniques for analyzing single-potential scattering[3] may be applied to portions of this data.

We begin in Sec. II by summarizing the relationships between the singlet and triplet scattering amplitudes and the differential cross sections for the scattering of atoms with polarized electrons from unpolarized target atoms (these cross sections were measured in I). In Sec. III we discuss the connection between the potentials and the scattering amplitudes, stressing the qualitative differences between the singlet and triplet scattering which are caused by the relationship between the potential well depth and the kinetic energy. Section IV contains an analysis of the probability of spin exchange based on the asymptotic behavior of the potentials. In Sec. V we determine parameters which characterize the minimum in the triplet potential by analyzing the rainbow scattering observed in I. Finally, in Sec. VI we discuss the contributions we have made to the understanding of the alkali-alkali potentials, and the problems which still remain.

The emphasis in this paper is more toward developing and discussing appropriate models than toward extracting numerical results from the data in I. This emphasis stems from our conviction that it is important to understand the connection between the potentials and the (predicted) cross sections. The results obtained in this paper are useful for two reasons: They provide good starting points for guessing the right potentials, and they provide us with intuition to guide us in modifying our guesses if they fail to reproduce the experimental results for the cross sections.

We use atomic units ($\hbar = e = m_e = 1$) throughout this paper. Table I gives conversion factors to various other units.

## II. SPIN-EXCHANGE FORMALISM

We are concerned here with spin-exchange collisions between atoms in $^2s$ states. These are treated by assuming that the interaction between the two atoms may be written in terms of two separate spherically symmetric potentials

$$V(r) = P_1 V_1(r) + P_3 V_3(r), \tag{1}$$

one for each possible value of total electron spin. ($P_1$ and $P_3$ are projection operators for the singlet and triplet configurations of the total electron spin of the molecule formed during the collision.) This interaction gives a scattering matrix

$$F(\theta) = P_1 f_1(\theta) + P_3 f_3(\theta), \tag{2}$$

where $f_1(\theta)$ and $f_3(\theta)$ are the singlet and triplet scattering amplitudes. Each scattering amplitude depends only on the corresponding potential, the energy, and the c.m. scattering angle $\theta$.

Underlying Eq. (1) is the assumption that the collision time is sufficiently short so that all inter-

TABLE I. Conversion factors (atomic units and other units).

| | Atomic units | Other units |
|---|---|---|
| angular momentum | $\hbar$ | $1.054\,592\times10^{-27}$ erg$^{-1}$sec$^{-1}$ [a] |
| charge | $e$ | $4.803\,25\times10^{-10}$ esu[a] |
| mass | $m_e$ | $9.109\,56\times10^{-28}$ g[a] |
| time | $\dfrac{\hbar^3}{m_e e^4}$ | $2.418\,85\times10^{-17}$ sec |
| length | $a_0 = \dfrac{\hbar^2}{m_e e^2}$ | 0.529 177 Å (1 Å $=10^{-8}$ cm |
| energy | $\dfrac{m_e e^4}{\hbar^2} = \dfrac{e^2}{a_0}$ | $4.359\,83\times10^{-11}$ erg<br>$=27.211\,64$ eV [b,c]<br>$=626.623$ kcal/mole<br>$=2.194\,747\times10^{5}$ cm$^{-1}$ |
| velocity | $\dfrac{e^2}{\hbar} = \alpha c$ | $2.187\,69\times10^{8}$ cm/sec[d] |
| wavelength of a particle $\lambda$ | | |
| $=0.287\,256\ (AE)^{-1/2}$ | | $\lambda$ in Å, $E$ in ev, $A$ = atomic number[b] |
| $=0.104\,061\,5\ (AE)^{-1/2}$ | | $\lambda$ in $a_0$, $E$ in a.u. |
| velocity of a particle $v$ | | |
| $=1.398\,149\times10^{6}\ (E/A)^{1/2}$ | | $v$ in cm/sec, $E$ in eV, $A$ is atomic number |
| $=\ .033\,123\,80\ (E/A)^{1/2}$ | | $v$ in a.u., $E$ in a.u. |

[a] Taken from Taylor *et al.*, Rev. Mod. Phys. 41, 375 (1969).

[b] 12 C = 12 taken as standard.

[c] 1 eV = 23.0278 kcal/mole = 8065.48 cm$^{-1}$.

[d] $\alpha$ is fine-structure constant and $c$ is speed of light.

actions between the singlet and triplet states may be neglected. In addition, this treatment requires that adiabatic conditions prevail throughout the collision. These two considerations restrict this analysis to collisions with kinetic energies between $10^{-4}$ and $10^{-1}$ a.u., comfortably bracketing the range of energies in the experiments in I.

The cross sections for various spin-dependent collision processes may be expressed in terms of the singlet and triplet scattering amplitudes.[4] For collisions with target atoms with electron spin $\frac{1}{2}$ and polarization $P$, Burnham[5] has shown that the cross section for electron spin exchange is (the angular dependence is not exhibited to simplify the expressions which follow)

$$\sigma(\uparrow\rightarrow\uparrow) = 2\,|\tfrac{1}{4}(f_1-f_3)|^2 - 2P\,|\tfrac{1}{4}(f_1-f_3)|^2, \tag{3}$$

while the cross section for scattering with no change of spin is

$$\begin{aligned}\sigma(\uparrow\rightarrow\uparrow) = {} & |\tfrac{1}{4}(f_1+3f_3)|^2 + |\tfrac{1}{4}(f_1-f_3)|^2 \\ & + P\,(|\tfrac{1}{2}(f_1+f_3)|^2 - |\tfrac{1}{4}(f_1+3f_3)|^2 \\ & - |\tfrac{1}{4}(f_1-f_3)|^2).\end{aligned} \tag{4}$$

Corresponding cross sections for initial spin "down" are the same, except that the sign of $P$ is reversed. (Burnham's results include a factor depending on the nuclear spin of the primary atom, but the results in I were corrected for this effect in I, so that we may ignore this complication here.)

In the differential spin-exchange measurements which have been made to date, the target beam has been unpolarized, making it impossible to determine $|f_1(\theta)+f_3(\theta)|^2$ independently of $|f_1+3f_3|^2$ and $|f_1-f_3|^2$. These measurements therefore determine an electron spin-exchange cross section

$$\sigma_{\mathrm{ex}}(\theta) = \tfrac{1}{8}\,|f_1(\theta)-f_3(\theta)|^2 \tag{5}$$

and a sum cross section [the sum of the cross sections in Eqs. (3) and (4) with $P=0$]

$$\sigma_{\mathrm{sum}}(\theta) = \tfrac{1}{4}\,|f_1(\theta)|^2 + \tfrac{3}{4}\,|f_3(\theta)|^2. \tag{6}$$

Our spin-exchange cross section is for scattering from an unpolarized target; the exchange cross section for a target with polarization opposite to the incident beam would be twice as large (if both beams were completely polarized). This factor of 2 has caused confusion in earlier work on total spin-exchange cross sections.[6]

$\sigma_{\mathrm{sum}}$ is the cross section which would be measured in an experiment which was not sensitive to the electron spin of the atoms. It contains no interference terms between the triplet and singlet scattering amplitudes, and is the weighted average of the singlet and triplet cross sections, each determined from the corresponding potential.

For some analytical purposes, the probability of exchange is a convenient auxiliary variable, especially since many types of apparatus errors do not affect it. This quantity is defined as

$$P_{\mathrm{ex}}(\theta) = \frac{\sigma_{\mathrm{ex}}(\theta)}{\sigma_{\mathrm{sum}}(\theta)} = \frac{|f_1(\theta)-f_3(\theta)|^2}{2|f_1(\theta)|^2+6|f_3(\theta)|^2} = \frac{1+x^2-2x\cos\delta}{6+2x^2}, \tag{7}$$

where

$$x(\theta) = |f_1(\theta)|/|f_3(\theta)|$$

and

$$\delta(\theta) = \arg[f_1(\theta)] - \arg[f_3(\theta)]. \tag{8}$$

Equation (7) shows that the probability of exchange depends only on the *relative* magnitudes and phases of the scattering amplitudes involved.

Although $P_{\mathrm{ex}}$ depends on both $x$ and $\delta$, it is frequently possible to determine separately both $x$ and

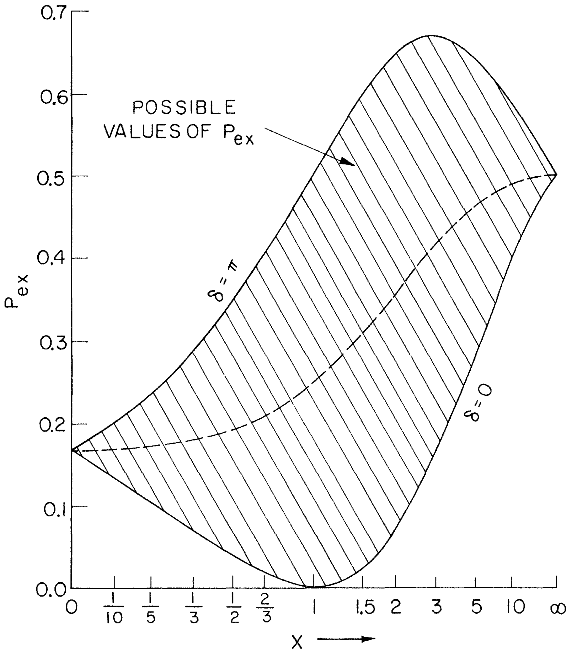

FIG. 1. Allowed values of $P_{ex}$ as a function of the relative magnitude $x$ and relative phase $\delta$ of the singlet and triplet scattering amplitudes. $P_{ex}$ is greatest when $\delta = \pi$ and smallest when $\delta = 0$. The dashed line gives the value of $P_{ex}$ when averaged over $\delta (0 \leq \delta \leq 2\pi)$.

$\delta$ from the data by studying the angular behavior of $P_{ex}$. This is because $\delta$ varies more rapidly with angle than does $x$, so that the value of $x$ acts as a constraint on the variations of $P_{ex}$ caused by the more rapid changes of $\delta$. The behavior of $P_{ex}$ is illustrated in Fig. 1, where the permissible values of $P_{ex}(x, \delta)$ are shown shaded. When $\delta = \pi, 3\pi, 5\pi, \ldots$, then $P_{ex}$ lies at the upper edge of the shaded region; when $\delta = 0, 2\pi, 4\pi, \ldots$, then $P_{ex}$ lies at the lower edge. If $P_{ex} = 0$, we can conclude immediately that $\delta = 2n\pi$ (with integral $n$) and that $x = 1$.

If $\delta$ changes rapidly (and smoothly) with angle, and the resultant oscillatory structure of $P_{ex}$ is averaged away either intentionally or due to poor apparatus resolution, then the value of $x$ may be determined from

$$\langle P_{ex}(\theta) \rangle_\theta = \tfrac{1}{2}(x^2 + 1)/(x^2 + 3), \tag{9}$$

if $x(\theta)$ changes slowly with angle. $\langle P_{ex} \rangle_\theta$ is the averaged value of $P_{ex}$ (over the oscillations caused by changes in $\delta$).

## III. SCATTERING AMPLITUDES

The cross sections are uniquely determined by the singlet and triplet scattering amplitudes [Eqs. (5) and (6)] which may be determined from the corresponding potentials. Accuracy sufficient to discuss the experiments in I may be obtained with the JWKB approximation and the standard partial wave analysis, but this approach does not provide us with any way to deduce the potentials from the scattering data, nor does it provide insight about which features of the potential influence which aspects of the cross sections.

The semiclassical approximation overcomes this difficulty and will be used throughout much of the analysis presented here. We assume that the reader is familiar with the classic paper by Ford and Wheeler,[7] as well as our note[8] on the significance of contributions from both positive and negative impact parameters. Some familiarity with work on rainbow scattering[3,9,10] would also be helpful.

While both the triplet and singlet potentials in alkali-alkali systems are attractive at moderate internuclear separations and repulsive at short ranges, there is a qualitative difference in the scattering which they produce in the thermal-energy collisions under study here. This difference arises because the singlet potential well depth is several times larger than the kinetic energy, whereas the opposite is true for the triplet well depth. The triplet state well depth is a small fraction ($\sim \frac{1}{8}$) of the kinetic energy, and the attractive deflections produced by the potential are < 1 rad (see Fig. 2). This leads to rainbow scattering which was discussed by Ford and Wheeler.[7,9] In contrast, the singlet well depth

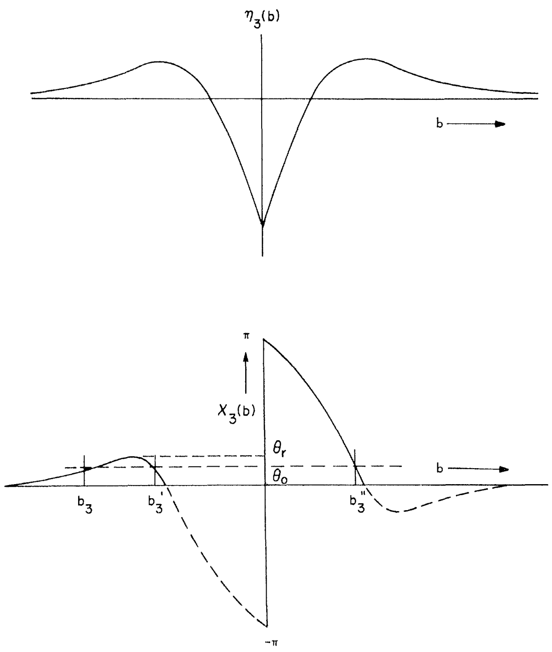

FIG. 2. Typical phase and deflection function for triplet state alkali scattering discussed in Sec. III. The long-range interaction is attractive; consequently, the principle contribution to scattering at the triplet rainbow angle $\theta_r$ comes from regions of negative impact parameters.

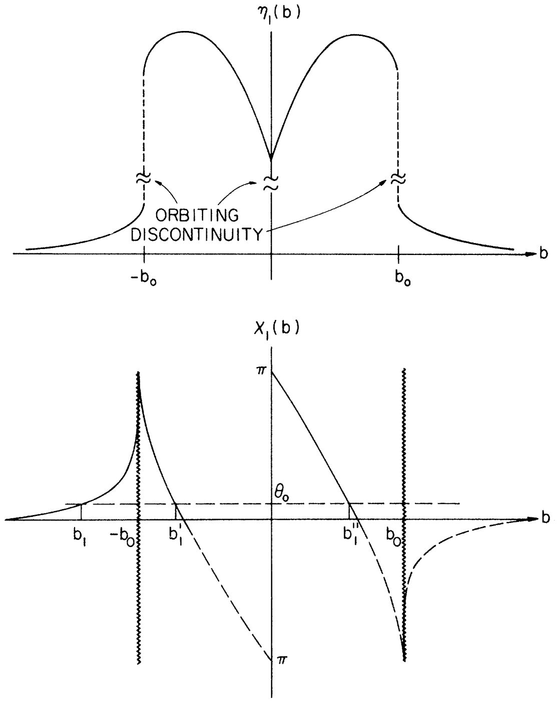

FIG. 3. Typical phase and deflection function for singlet-state alkali scattering discussed in Sec. III. The discontinuity in the phase at $\pm b_0$ is caused by orbiting, and the deflection function is not defined at these points.

(determined from molecular spectra)[11] is several times larger than the kinetic energy in these experiments. This leads to collisions in which the attractive portion of the potential overcomes the centrifugal barrier, causing a discontinuity in the phase function $\eta_1(b)$ (see Fig. 3). This results in orbiting collisions, and no rainbow is observed.

### A. Triplet Scattering Amplitude

The phase function for scattering from a typical alkali-alkali triplet potential at thermal energy is shown in Fig. 2. (The maximum phase would be several radians and would occur for impact parameters near $10a_0$.) The classical deflection function [Eq. (9)] for this phase function is also shown. It is clear that for angles like $\theta_0$, which are smaller than $\theta_r$, there will be three impact parameters which contribute to the triplet scattering amplitude [that is, there will be three values of $b$ which satisfy $\chi(b) = \theta_0$]. Thus, we write (for angles smaller than $\theta_r$)[9]

$$f_3(\theta) = f_3(b_3(\theta)) + f_3(b'_3(\theta)) + f_3(b''_3(\theta)). \tag{10}$$

The magnitude of each contribution depends on $(dx/db|_{b=b_i})^{-1/2}$, so that $f_3(b_3)$ will have the largest amplitude, especially at small angles. $b_3$ and $b'_3$ correspond to trajectories with dominantly attractive interaction, while the interaction along the trajectory with impact parameter $b''_3$ is dominantly repulsive. At angles larger than $\theta_r$, the contributions from attractive scattering vanish and $f_3(b''_3)$ is the only contribution to the scattering amplitude. Near the rainbow angle $\theta_r$, the contributions from $b_3$ and $b'_3$ merge and this analysis no longer applies.

### B. Singlet Scattering Amplitude

The phase function for the singlet state scattering is qualitatively different from the triplet phase function in that there is a discontinuity at the impact parameter $b_0$ (and also $-b_0$; see Fig. 3). The classical trajectories of particles with impact parameter less than $b_0$ are drawn into the deep part of the potential and accumulate considerable extra phase; the centrifugal barrier is sufficiently strong to prevent this from happening to the trajectories of particles with impact parameters larger than $b_0$. (Actually, there is some chance of quantum tunneling through the barrier. This effect has been shown to be negligible. Furthermore, the JWKB approximation has been shown to be adequate in the neighborhood of the singularity.)[12]

The classical deflection function (see Fig. 3) has an orbiting singularity associated with the discontinuity in the phase function. As a result, there are trajectories with impact parameters near both $b_0$ and $-b_0$ which scatter to all final angles. Consequently, there are five impact parameters which contribute to the singlet amplitude at any angle $\theta_0$ (see Fig. 3):

$$f_1(\theta) = f_1(b_1(\theta)) + f_1(b'_1(\theta)) + f_1(b''_1(\theta)) + f_1(b_0) + f_1(-b_0). \tag{11}$$

As in the triplet scattering, the contribution from $b_1$ dominates, especially at small angles. The contributions from the orbiting impact parameters ($b_0$ and $-b_0$) are similar to those caused by diffraction and they are generally small. The two contributions from $b'_1$ and $b''_1$ are not only smaller than $f(b_1)$ but have a very large phase relative to $f(b_1)$ because of the discontinuity in $\eta(b)$. These considerations make it very difficult to observe interference effects in the singlet cross section $\sigma_1(\theta)$, and we have not found any evidence of it in the data in I.

### C. Summary

In this section we have used the semiclassical approximation to express both singlet and triplet scattering amplitudes as sums of contributions from distinct impact parameters. Since it is not possible to determine the impact parameter before the collision, there are several distinct contributions to the amplitudes, and the cross sections show oscillatory interference patterns similar to those found in the multislit diffraction of monochromatic light.[8] This is one of the most interesting features of these experiments, since the interpretation of the interference structure leads directly to knowledge of the potential. The interference is not confined to each scattering amplitude individually; since the scattering system is not prepared in a pure singlet or triplet state, a further interference effect is observed between the singlet and triplet amplitudes (i.e., among their components). This produces an oscillatory structure in the spin-exchange cross section (and also in the probability of exchange).

## IV. PROBABILITY OF EXCHANGE

The probability of exchange [Eq. (7)] depends only on the phase difference $\delta$ and the relative magnitude $x$ ($x=|f_1|/|f_3|$) of the singlet and triplet scattering amplitudes. It is a sensitive function of any difference between the two potentials, since $P_{\text{ex}}$ would be 0 everywhere if the potentials (and, consequently, $f_1$ and $f_3$) were identical. In this section we develop approximations which permit us to determine $\delta$ from the difference potential [see Sec. VI, Eq. (23)], and we develop approximate techniques for finding $\delta$ from the data on $P_{\text{ex}}$. These procedures permit a direct comparison of theory and experiment, a comparison which is facilitated by comparing theoretical and experimental results for $v_{\text{rel}}\delta$ versus $E\theta$. (These are called "reduced variables"[13]; we will use the symbol $\tau=E\theta$ for the reduced angle, and $v\delta$ for the reduced phase.)

### A. Approximations to Amplitudes

In order to relate the potentials to the probability of exchange, we first simplify the expressions for the singlet and triplet scattering amplitudes [Eqs. (10) and (11)]. To obtain a first approximation, we replace each amplitude by its dominant contribution [$f_1(b_1)$ and $f_3(b_3)$, respectively], so that

$$f_1(\theta)\approx f_1(b_1(\theta)), \tag{12a}$$

$$f_3(\theta)\approx f_3(b_3(\theta)). \tag{12b}$$

This approximation will fail for angles larger than the triplet rainbow angle $\theta_r$ [where $|f_3(b_3'')|\gg|f_3(b_3)|$], and also near this rainbow angle [where $f_3(b_3')$ runs together with $f_3(b_3)$]. At angles smaller than the triplet rainbow, however, the approximation should be fairly good.

### B. Theoretical Expression for Phase Difference

Since the singlet and triplet potentials are nearly equal at large impact parameters [like $b_1(\theta)$, and $b_3(\theta)$], we can make use of results which are valid when the difference potential is smaller than the average potential, i.e., $\Delta V/V_w \ll 1$. [See Sec. VI for a discussion of the difference potential $\Delta V=V_3-V_1$, and the average potential, $V_{\text{av}}=\frac{1}{2}(V_3+V_1)$, which equals the van der Waals potential $V_w$ in this case.] The most important such result gives an expression for $\delta$ directly in terms of the difference potential,[14,8]

$$\delta(\theta,v)\approx(1/\hbar v)\left[\int_{\bar{b}}\Delta V(r)\,dz\right]\times\left[1+\mathcal{O}(\Delta V(\bar{b})/2V_w(\bar{b})\right], \tag{13}$$

where $\mathcal{O}$ means "order of." This expression is based on an impact approximation to the phase; the integral in Eq. (13) [and Eq. (16) also] is a straight-line integral with impact parameter $\bar{b}(\theta)$ equal to the average of $b_1(\theta)$ and $b_3(\theta)$: $\bar{b}(\theta)=\frac{1}{2}[b_1(\theta)+b_3(\theta)]$.

The value of $\delta$ is of prime importance in determining $P_{\text{ex}}$ [see Eq. (7)] since $x(b)$ generally varies slowly or has a known value. Such is the case when $\Delta V/V_w \ll 1$: Then $x$ is nearly equal to unity. It has been shown[15] that when $\Delta V$ and $V_w$ obey inverse power laws (or may be approximated by them in the region of interest):

$$x(\bar{b})=1-\alpha((\Delta V(\bar{b})/V_w(\bar{b}))+\quad([\Delta V(\bar{b})/V_w(\bar{b})]^2), \tag{14}$$

where $\alpha$ depends only on the exponents in the inverse power laws. Hence, at small angles, where $\bar{b}(\theta)$ is large, $x$ approaches unity [since $\Delta V(b)$ decreases exponentially for large $b$]. Under these circumstances the familiar result[14]

$$P_{\text{ex}}\approx\tfrac{1}{2}\sin^2(\tfrac{1}{2}\delta) \tag{15}$$

applies, emphasizing the oscillatory behavior of the probability of exchange.

The average impact parameter $\bar{b}(\theta)$ can be determined from the average potential, which equals the van der Waals potential in our model of the potentials [see Eq. (25)]. We use the first-order impact approximation to find the average deflection function $\chi_w(b)$

$$\chi_w(b,E)=(b/E)\int_{\bar{b}}dz\,[V_w'(r)/r], \tag{16}$$

where $V'(r)$ is $dV(y)/dy\,|_{y=r}$.

Equations (13) and (16) both depend on straight-line approximations to the trajectory; hence, changes in relative velocity (or energy) affect only the time scale. (This would not be true if a higher-order impact approximation[13] were used.) Since the effects of relative velocity and energy are eliminated by plotting $v\delta(\theta,v)$ versus $\tau$, as can be seen from Eqs. (13) and (16), these are naturally chosen as reduced variables. If experimental data taken at different velocities agree with each other when plotted with these variables, then that is evidence for the applicability of the impact approximation and our "dominant-contribution" approximation to the amplitudes – even if the experimental results disagree with predictions made from particular expressions for the potentials.

In Figs. 4–8 we show theoretical calculations

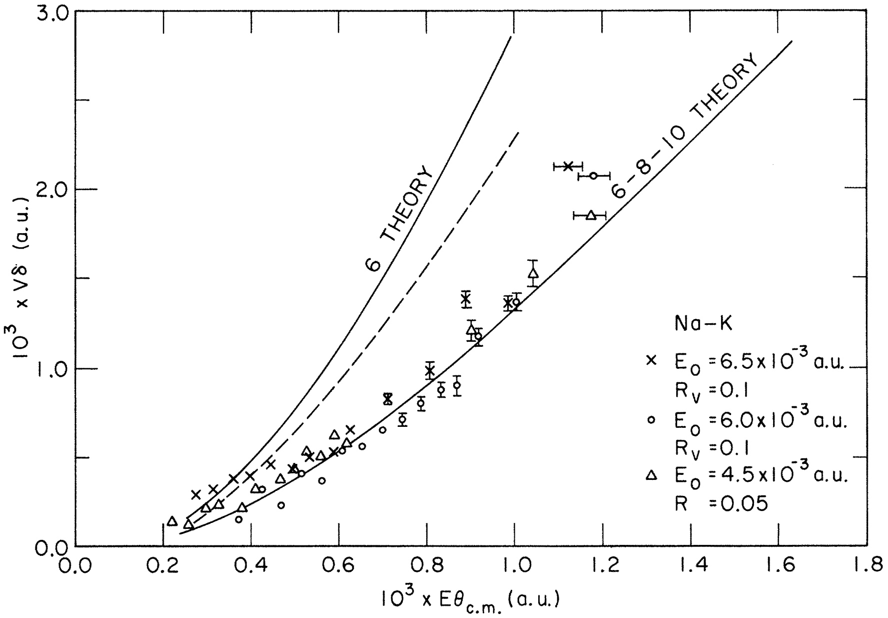

FIG. 4. $v\delta$ versus $\tau$ for Na-K. The solid lines were calculated with the DR difference potential, while the KR difference potential was used for the dashed lines. See Sec. IV for complete explanation.

for $v\delta$ versus $\tau$ as solid or dashed lines. These calculations were made with the impact approximations described above, and are therefore independent of the relative velocity of the collision. Up to five curves are shown in each of the systems Na-K, Na-Rb, Na-Cs, K-Rb, and K-Cs, corresponding to different estimates of the asymptotic behavior of the potential.

The asymptotic potential depends on two separate theoretical calculations: one for the difference potential and another for the van der Waals potential. There are several theoretical calculations for both of these, so it is possible to obtain many different predictions for $v\delta(\tau)$ by combining them in various ways. We have obtained a family of predictions (solid curves in Figs. 4–8) by combining four different estimates for the van der Waals potential with the Dalgarno-Rudge (DR)[16] estimate for the difference potential [see Eq. (24)]. ($\Delta V_{\mathrm{DR}}$ is the smallest of the calculations of the difference potential.) In addition, we have made one prediction (dashed line in Figs. 4–8) based on the Knox-Rudge (KR)[17] estimate for the difference potential ($\Delta V_{\mathrm{KR}}$ is the largest of all difference potential calcula-

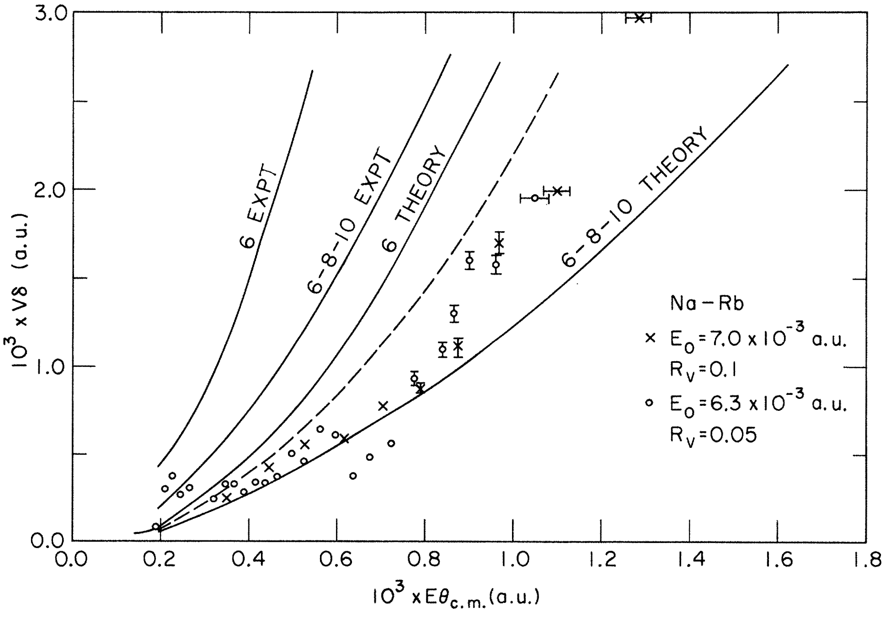

FIG. 5. $v\delta$ versus $\tau$ for Na-Rb.

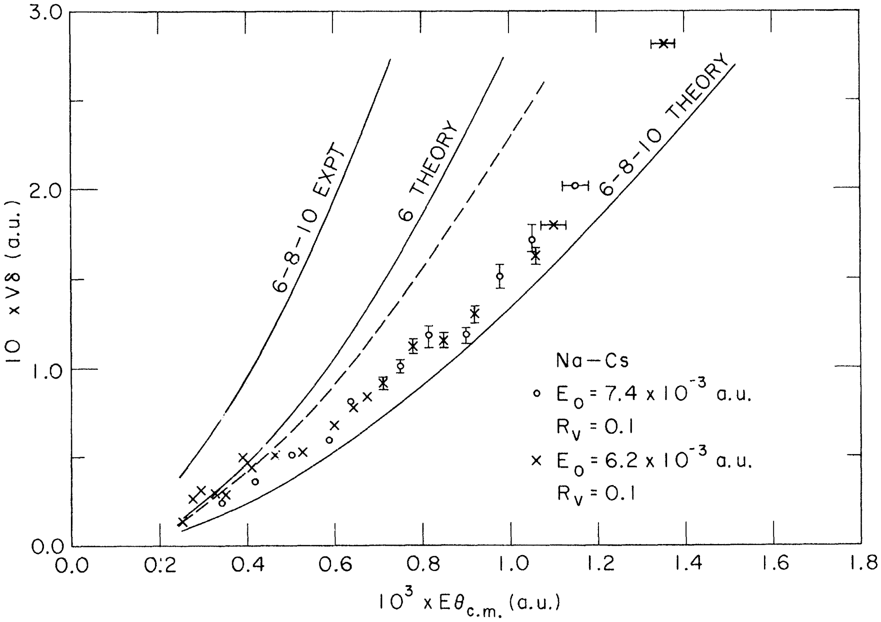

FIG. 6. $v\delta$ versus $\tau$ for Na-Cs.

tions); the largest estimate for the van der Waals potential was used for this.

It is clear from Figs. 4–8 that the differences among the several possible van der Waals potentials cause much more variation in the predicted $v\delta(\tau)$ than do the discrepancies in the difference potentials. (The dashed curve was calculated with the same van der Waals potential as the lowest solid curve; the solid curves were all calculated with the same difference potential.) While this is partly because our model is more sensitive to the van der Waals potential, it also reflects the greater range of possibilities for this potential.

Part of the variation in the van der Waals potential [Eq. (22)] comes from uncertainty in the leading term $C_6$: Recent theoretical calculations by Dalgarno and Davison (DD)[18] are roughly twice as large as earlier experimental results by Buck and Pauly.[19] We have labeled curves calculated with Dalgarno and Davison's values "theory" and those with Buck and Pauly's values "expt." The remainder of the uncertainty in the van der Waals interaction comes from higher-order terms in the van der Waals interaction. In alkali-alkali systems these

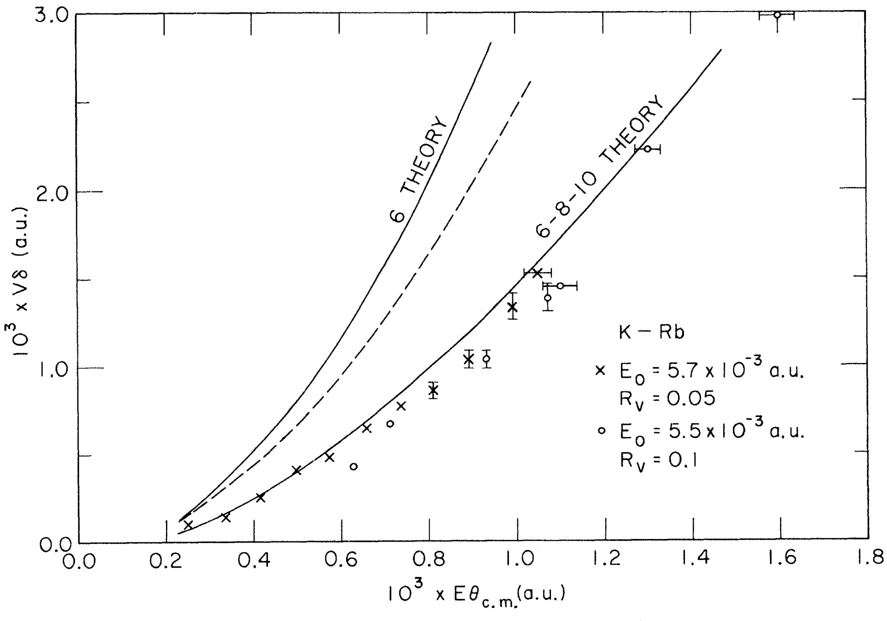

FIG. 7. $v\delta$ versus $\tau$ for K-Rb.

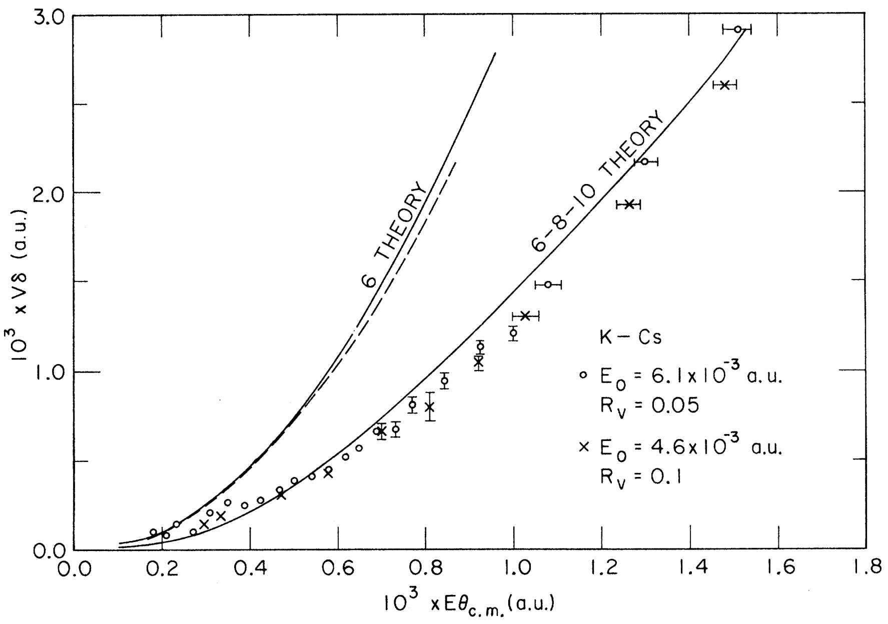

FIG. 8. $v\delta$ versus $\tau$ for K-Cs.

terms ($C_8R^{-8}$, $C_{10}R^{-10}$) are quite large and contribute significantly to the interaction in the region near $r = 15a_0$, where our measurements of $P_{ex}$ are most sensitive to the potential. As explained in Sec. VI of this paper, we use Davison's[20] values for $C_8/C_6$, and we find the ratio $C_{10}/C_6$ from Fontana's work.[21] When included in the van der Waals interaction potential, these terms change our prediction of $v\delta(\tau)$ considerably, so we have made calculations both with and without them. Curves for $v\delta(\tau)$ in Figs. 4–8 with both higher-order terms are designated "6-8-10," while those with only the leading term are designated simply "6." Using both experimental[19] and theoretical[18] values of $C_6$, we have calculated curves both with and without the correction terms (see Figs. 4–8). (We have not made calculations with the eighth-power correction term alone, because we do not feel that there is any justification for including only some of the higher-order terms.)

### C. Experimental Results for the Phase Difference

Now that we have described how $\delta$ may be calculated from the potentials, let us turn to the problem of extracting $\delta$ from the data on $P_{ex}$. The measurements in I were made at relatively low velocities so that $\delta$, which contains the factor $1/v$, varies rapidly relative to $x$ and is responsible for the oscillatory structure in $P_{ex}$. [We are implicitly assuming our dominant-contribution approximation to the amplitudes in this discussion; see Eq. (12).] Hence, we can locate the angles at which $\delta$ is a multiple of $\pi$ from the extrema in $P_{ex}$, and we can find the angles for which $\delta$ is an odd multiple of $\frac{1}{2}\pi$ from the points where $P_{ex}$ passes through its average value [see Eq. (9)]. This method has the advantage that averaging processes in the apparatus are unlikely to change the position of these points (although the amplitude of the oscillations may be reduced). This procedure determines four angles, with the corresponding value of $\delta$, for each full cycle of oscillation observed in $P_{ex}$ past the first maximum, and it has been used to determine the points with horizontal error bars in Figs. 4–8.

At small angles $\delta \rightarrow 0$, since $\Delta V(r)$ decreases exponentially for large $r$ [see Eqs. 24) and (13)]. Since $x \rightarrow 1$ under these circumstances [see Eq. (14)], we expect that Eq. (15) will apply; consequently, $P_{ex}$ should vanish for small angles if the dominant-contribution approximation is valid. The experimental data in I shows that $P_{ex}$ does decrease to $\lesssim 0.01$ in all systems studied. This indicates that our model is working, and it shows that $x(\theta = 0) = 1.0 \pm 0.2$; otherwise it is not possible for $P_{ex}$ to be less than 0.01; see Fig. 1. Consequently, Eq. (15) does apply, as asserted above.

Consider the problem of determining $\delta$ from $P_{ex}$. At small angles we have shown that $x = 1.0$, so that Eq. (15) may be used to find $\delta$ directly. At larger angles we expect $x$ to decrease [see Eq. (14)]; we can find its value at the maximum of $P_{ex}$ by noting that this maximum occurs when $\delta = \pi$ in Eq. (7) (assuming that $\delta$ changes much faster than $x$). This value of $x$ (generally $\sim 0.8$ for the data in I) may now be used in Eq. (7) to determine $\delta$ from $P_{ex}$ in the region near its maximum.

To find $\delta$ at points between the small angles where $x \cong 1.0$ and the larger angle where $P_{ex}$ is maximum (and $x \cong 0.8$) we can use either Eq. (15) or Eq. (7) (with the appropriate value of $x$). These two formulas give results which differ by only a little more than the statistical error (except near the ends of the region where we know which formula is correct). To improve these estimates we assume that the quotient $v\delta/E\theta$ is proportional to $\Delta V/V_w$, which enables us to estimate $x(\theta)$ from Eq. (14). [This rather crude approximation is based on Eqs. (13) and (16).] This permits us to solve Eq. (7) for $\delta$ in the entire range from $\theta = 0$ to the first maximum in $P_{ex}$. Errors in our crude approximation for $\Delta V/V_w$ affect the value of $x$ only weakly, since the entire correction is at most 0.2, and the error introduced by this whole procedure is considerably smaller than the statistical errors in the experiment.

The values of $\delta$ estimated from our data by this procedure are shown in Figs. 4–8. It is clear that in each system the results obtained for $v\delta(\tau)$ are quite independent of the energy. We feel that this is strong evidence that our methods of analysis are valid (as well as another example of the utility of reduced variables).

### D. Comparison of Theory and Experiment for $v\delta(\tau)$

It is clear from Figs. 4–8 that our analysis of the data in I is most compatible with the DR calculation of the difference potential together with the largest possible van der Waals interaction – the theoretical value of $C_6$ plus eighth- and tenth-power correction terms. All other combinations give predictions for $v\delta(\tau)$ which are considerably higher than the data (except possibly in Na-Rb).

We believe that the above comparison is significant only in the region $4\times10^{-4} < \tau < 10^{-3}$, even though the agreement extends over a greater range in some systems. The upper limit is set by the breakdown of the assumption $\Delta V/2V_w \ll 1$, which was required in the impact approximation for the phase difference [Eq. (13)]. The value of $\Delta V(\tilde{b})/2V_w(\tilde{b})$ (where $\tilde{b}$ is the impact parameter for reduced deflection $\tau = 10^{-3}$) is $0.2 \pm 0.05$ for all the systems in I (assuming the potentials described in the preceding paragraph). The experimental determination of $\delta$ in the region $\tau > 10^{-3}$ should be quite good, and it would be interesting to see if the experiment agreed with a more complete theoretical calculation. Unfortunately, such a calculation (e.g., a calculation of the scattering amplitudes by partial-wave analysis) would involve values of the potentials at small internuclear separations and would therefore be sensitive to potential parameters other than those which determine the asymptotic behavior of the potentials.

At small angles (and, consequently, for small values of $\tau$) where $P_{ex}$ is small, our dominant-contribution approximation to the scattering amplitudes [Eq. (12)] fails for the exchange amplitude, because the dominant contributions to the singlet and triplet amplitudes, $f_1(b_1)$ and $f_3(b_3)$, become nearly equal, so that their difference approaches 0. The neglected contributions to the scattering amplitudes then become important, since they prevent $\sigma_{ex}$ [Eq. (5)] from vanishing as our simple theory predicts. This accounts for the tendency for the experimental values of $P_{ex}$ to lie slightly above 0 at small angles, and it therefore invalidates our determination of $\delta$ from the data at these small angles.

The residual contributions to the amplitudes also cause a small oscillation of $\delta(\tau)$. These oscillations are visible in the Na-Cs data [Fig. (6)], and may contribute to the roughness of the Na-Rb data. We feel that $f_3(b_3')$ and $f_3(b_3'')$ are the largest residual amplitudes [$f_3(b_3')$ should cause slower oscillations than $f_3(b_3'')$]. While accurate calculations using the entire potentials should reproduce the small-angle structure in $P_{ex}$, our determination of $\delta$ from the data fails as $\delta$ approaches 0, because small variations in $x$ caused by the residual contributions become important there.

In spite of the limitations of the model for $\tau \lesssim 0.4\times10^{-3}$ and for $\tau > 10^{-3}$, it should work reasonably well in between. We have checked it against a computer calculation which used the JWKB approximation for the phases and which summed partial waves up to $l = 1500$. Using (LJ)(8–6) potential for both $V_1$ and $V_3$, we computed $P_{ex}(\tau)$. This was then analyzed (as if it were experimental data) to find $v\delta(\tau)$, which was compared with our impact parameter calculations [Eqs. (13) and (16) using $\frac{1}{2}(V_1 + V_3)$ for the van der Waals potential]. We obtained 10% agreement for $3\times10^{-4} < \tau < 10^{-3}$ a.u.

One noteworthy feature of both the data and all the calculations is that $v\delta(\tau)$ is nearly independent of the alkalis which are involved. The data for K-Rb and K-Cs do lie slightly below the data for the systems containing Na, but in no case is the variation between systems as large as 10%. This similarity of the theoretical predictions is illustrated in Fig. 9, where we compare various alkali-alkali systems. Using the theoretical $C_6$ plus both higher-order terms with either the DR (solid lines) or KR (dashed lines) difference potential produces such similar results for the systems studied in I that only the limiting curves can be shown. The theoretical predictions for $v\delta(\tau)$ in the systems K-Rb and K-Cs are slightly higher than those for systems containing Na, in contrast to the experimental data. While predictions of $v\delta(\tau)$ using $\Delta V_{KR}$ are generally about 80% above the corresponding predictions made with $\Delta V_{DR}$, this is not the case for systems which contain Li. For this reason, studies of Li-containing systems would be helpful in deciding which calculation better describes the variation of $\Delta V$ in various alkali-alkali systems.

The similarity of the $v\delta(\tau)$ curves for the various alkali-alkali systems serves as a reminder that $v\delta(\tau)$ depends on two quantities: the difference potential $\Delta V(r)$ and the van der Waals potential $V_w(r)$. If $\Delta V(r)$ is increased, then the plot $v\delta(\tau)$ will rise; however, if $V_w(r)$ is increased, then the curve will

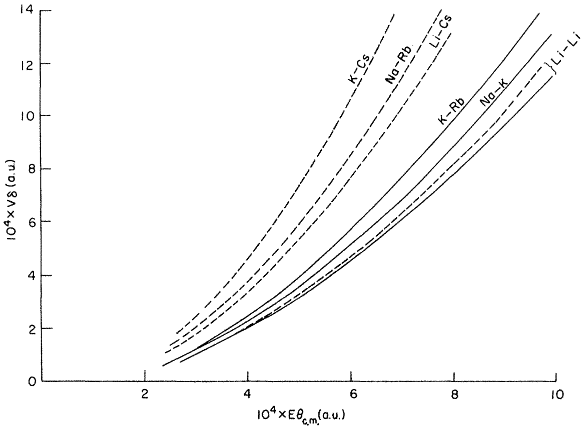

FIG. 9. Comparison of theoretical estimates of $v\delta$ versus $\tau$ for various alkali-alkali systems. Theoretical values of $C_6$, $C_8$, and $C_{10}$ were used for the van der Waals interaction.

be displaced outward, effectively lowering $v\delta(\tau)$. Both $\Delta V$ and $V_w$ increase for heavier alkalis (at $r = 15a_0$, $V_w$ for K-Cs is more than twice $V_w$ for Na-K), and hence $v\delta(\tau)$ is similar even for quite different systems. Comparison with our experiment does not check both theoretical calculations independently; rather it checks a sort of ratio between the two.

In order to judge the implications of the comparison of the two theoretical calculations, we must consider the sensitivity of the $v\delta(\tau)$ curve to variations in both $\Delta V(r)$ and $V_w(r)$. Variations in $\Delta V(r)$ affect only $\delta$ [see Eqs. (13) and (16)], and the effect is linear. Variations in $V_w(r)$ affect the results in a more complicated fashion, since they cause variations in the impact parameter $\bar{b}(\tau)$, deduced from Eq. (16). The variations in $\bar{b}$, in turn, influence the value obtained for $v\delta(\tau)$ [see Eq. (13)]. Since $\Delta V(r)$ varies more rapidly with changes in $r$ than does $V_w(r)$, variations in $V_w$ cause exaggerated response in the $v\delta(\tau)$ curves: For impact parameters and values of $\tau$ typical of the data in I, a given fractional variation in $V_w$ will produce twice as much fractional variation in $v\delta(\tau)$. As an example, consider the theoretical curves in Fig. 5 for Na-Rb. In this system, $\Delta V_{\mathrm{KR}}$ is 60% higher than $\Delta V_{\mathrm{DR}}$; consequently, the $v\delta(\tau)$ curve which uses $\Delta V_{\mathrm{KR}}$ (dashed line) lies 60% above the calculation made with $\Delta V_{\mathrm{DR}}$. Comparison of the 6-8-10 theory and 6-8-10 expt curves shows the sensitivity of $v\delta(\tau)$ to changes in the van der Waals interaction: $V_w$ is 80% larger using the theoretical $C_6$, but $v\delta(\tau)$ is 180% larger when the experimental $C_6$ is used. Lowering $V_w$ by the factor 1.8 increases $v\delta(\tau)$ by the factor 2.8.

The experimental values of $v\delta(\tau)$ lie lower than all theoretical predictions except the one made by combining the smallest value of $\Delta V$ (DR) with the largest possible $V_w$ [(DD) plus eighth- and tenth-power correction terms], which is in fair accord with experiments. This is not an independent confirmation of both calculations, rather it has the following meaning: Any adjustment of $\Delta V$ towards larger (smaller) values must be compensated by a corresponding increase (decrease) in $V_w$ in order to retain agreement with the data in I. [Since $v\delta(\tau)$ is more sensitive to $V_w$ than to $\Delta V$, the fractional adjustment of $V_w$ will have to be only about 50% of the fractional change in $\Delta V$ in order to preserve the present agreement.]

Since $\Delta V_{\mathrm{DR}}$ is the smallest of all calculations of the difference potential, it seems unlikely that the correct $\Delta V$ is smaller than $\Delta V_{\mathrm{DR}}$. Thus the theoretical 6-8-10 van der Waals interaction represented a lower bound on the correct van der Waals interaction. Consequently, we feel that our experiment supports the values of $C_6$ calculated by Dalgarno and Davison,[18] while it disputes those found by Buck and Pauly[19] and by Fontana.[21]

It is tempting to claim that the experimental results definitely confirm the existence of eighth- and tenth-power terms in $V_w(r)$. While we believe that these terms are important, it would be possible to reproduce the data over these moderate ranges of $\tau$ by increasing $C_6$ roughly 50%, while setting $C_8$ and $C_{10}$ equal to 0. Definite confirmation of the existence of higher terms in $V_w(r)$ must await more detailed calculations of $v\delta(\tau)$ (e.g., calculations in the region $\tau > 10^{-3}$).

## V. SUM CROSS SECTION

### A. Explanation of Structure

The sum cross section [Eq. (6)] contains no interference terms between $f_1$ and $f_3$, and may be regarded simply as a weighted average of independent singlet and triplet cross sections:

$$\sigma_{\mathrm{sum}}(\theta) = \tfrac{1}{4}\sigma_1(\theta) + \tfrac{3}{4}\sigma_3(\theta) \tag{17}$$

with

$$\sigma_j(\theta) = |f_j(\theta)|^2, \quad j = 1, 3. \tag{18}$$

Obviously, features observed in $\sigma_{\mathrm{sum}}$ can come from either $\sigma_1$ or $\sigma_3$, or both, and additional information is necessary to determine the origin of the structure observed in $\sigma_{\mathrm{sum}}$ in Figs. 3-7 of I.

In measurements of the energy dependence of the total (integrated over all angles) sum cross section with kinetic energy between 0.5 and 100 a.u., Neumann and Pauly[22] ascribed the structure which they observed to the singlet interaction, because the triplet interaction (well depth ~ $10^{-3}$ a.u.) is too weak to produce sizeable effects in the energy range of their experiment. In the energy range of our experiments ($\leq 10^{-2}$ a.u.), however, the triplet interaction is important and $\sigma_3(\theta)$ displays considerable structure.

Surprisingly, the singlet interaction is so strong that no structure in $\sigma_1(\theta)$ can be observed in our experiment. This is due primarily to the finite energy resolution in our apparatus: Since the magnitude of the discontinuity in the singlet phase function changes with energy, the interference among $f_1(b)$ and the other contributions to the singlet amplitude [Eq. (11)] is washed out. (The most promising region in which to see the effects of such interference in $\sigma_{\text{sum}}$ would be past $\theta_r$, where $\sigma_3$ is small. There is no evidence of interference structure in $\sigma_1$ in the data in I, however.) Hence, we attribute all the structure observed in $\sigma_{\text{sum}}$ to the triplet cross section $\sigma_3$.

Before extracting information about the triplet potential from the structure in $\sigma_{\text{sum}}$, we first make a small subtractive correction to eliminate the $\frac{1}{4}\sigma_1$ from $\sigma_{\text{sum}}$ [see Eq. (17)]. To do this we fit the sum cross section with a curve of the form $\theta^{-7/3}$ at small angles. (This small angle behavior is expected[3] since both potentials go as $C_6 r^{-6}$ at large distances, and it is generally observed – see Fig. 7 in I.) By assuming that the singlet cross section follows this law up to $\tau = 2\times10^{-3}$, we can find $\sigma_3$ from Eq. (17). In practice, this procedure produces a very slight shift in the angle of the maxima and minima in the triplet cross section, because this structure is fairly sharp.

All of the sum cross sections in Figs. 3–7 of I exhibit pronounced maxima near $\tau = 1.7\times10^{-3}$ a.u. These maxima are relatively broad, the cross section oscillates at smaller angles, and it falls off sharply at larger angles. (See Figs. 3–7 in I). This behavior is characteristic of rainbow scattering,[7] (as is the fact that the value of $\tau$ at the maximum does not change when $E$ is varied), and we feel confident that these maxima result from rainbow scattering in the triplet state.

Further evidence for this is the low value of $P_{\text{ex}}$ at all the rainbow maxima. If a maximum occurs in the triplet scattering, then $x = |f_1|/|f_3|$ should be less than 1.0, limiting the maximum possible value for $P_{\text{ex}}$ (see Fig. 1). The range of values of $P_{\text{ex}}$ at the rainbow for all the data in I is $0.1 \leqslant P_{\text{ex}}(\tau_r) \leqslant 0.3$. Assuming that $x$ is the same for all systems and that this range is caused by variations in $\delta$ forces one to conclude that $x \approx 0.4$. The largest value of $P_{\text{ex}}$ observed in I at the rainbow maximum is 0.30 for K-Cs (at $E_0 = 6.1\times10^{-3}$ a.u.). Since there is a local maximum in $P_{\text{ex}}$ at this angle, we can set $\delta \approx 3\pi$, and solve Eq. (7) for $x$, with the result $x = 0.4$, in accord with the previous estimate. Comparing Eqs. (8) and (18) we see that $\sigma_1 \sim x^2\sigma_3 \sim 0.16\,\sigma_3$ in the neighborhood of the triplet rainbow.

Rainbow scattering occurs when the deflection function has an extremum (at the classical rainbow angle, $\theta_r$ in Fig. 2 for example). In the semi-classical approximation this leads to a maximum in the cross section located at a slightly smaller angle than $\theta_r$. $\theta_r$ is determined principally by the well depth of the triplet potential, which may be seen from the following argument. The angle of deflection is proportional to the impulse divided by the momentum which is (force) (time)/$(mv)$, or

$$\theta \approx \frac{(\text{force})/(\text{time})}{(\text{momentum})} \approx \frac{\epsilon}{R}\,\frac{R}{v}\,\frac{1}{mv} = \frac{\epsilon}{E}\,, \tag{19}$$

where $R$ is the size of the potential and $\epsilon$ is its depth. Hence, $\theta_r$ does not depend on the steepness of the potential. Accurate impulse approximations[3] yield

$$\theta_r = G\epsilon/E\,, \tag{20}$$

where $G$ is a numerical factor which varies from 1.79 to 2.10 for (LJ) $(n-6)$ potentials of the form

$$V(r) = \frac{\epsilon}{n-6}\left[6\left(\frac{r}{r_m}\right)^n - n\left(\frac{r}{r_m}\right)^6\right], \tag{21}$$

as $n$ varies from 7 to 14.

At angles such as $\theta_0$ in Fig. 2, which are smaller than the triplet rainbow angle, the triplet cross section shows oscillatory structure due to interference of both $f_3(b_3')$ and $f_3(b_3'')$ with the dominant contribution to the triplet scattering amplitude $f_3(b_3)$. Since $b_3''$ and $b_3$ are widely separated, the oscillations which result from the interference of $f_3(b_3)$ and $f_3(b_3'')$ will be quite rapid (they are called "rapid" or "secondary" oscillations). These are generally too rapid to be resolved without very good energy resolution (several percent), and they are not observed in the data presented in I except at small angles (see the data on K-Cs, Fig. 7 in I).

The oscillations due to interference between $f_3(b_3')$ and $f_3(b_3)$ have a relatively long period (typically, 0.1 rad) and are easily resolved in the sum cross sections presented in I; these oscillations are called supernumerary rainbows. The period of these oscillations depends on $\lambda$ and the distance between $b_3$ and $b_3'$,[8] and the supernumerary rainbow structure therefore depends strongly on the curvature of the potential near the bottom of the well. If the curvature is large, then the peak in the deflection function $\chi_3(b)$ for negative $b$ will be narrow, $b_3$-$b_3'$ will be small, and the period will be large. The supernumerary rainbow structure depends very weakly on the average value of $b_3$ and $b_3'$, and, consequently, little can be learned about the overall size of the potential from rainbow and supernumerary rainbow data.

### B. Triplet Well Parameters

We have used the tables of Hundhausen and Pauly[21] to determine triplet potential parameters from the location of the observed maxima and minima in $\sin(\theta)\sigma_3(\theta)$. We have tabulated (Table II) $\epsilon$ and $r_m$ (the depth and position) of the triplet wells in each of the systems studied, and in addition have tabulated

TABLE II. Values of $\epsilon$, $r_m$, and $d^2V/dr^2$ for alkali-alkali triplet potential determined from our rainbow data using both 8-6 and 12-6 potentials.

| System | $10^4\times V_f$ | $10^3\times E_0$ | $10^4\times\epsilon$ | | $r_m$ | | $10^4\times d^2V/dr^2\|_{r_m}$ | |
|---|---|---|---|---|---|---|---|---|
| | | | 8-6 | 12-6 | 8-6 | 12-6 | 8-6 | 12-6 |
| Na-K | 6.9 | 8.0 | 9.7±0.5 | 9.1±0.5 | 13.9±2.4 | 15.0±2.8 | 2.4±0.8 | 2.9±1.0 |
| | 6.0 | 6.2 | 9.8±0.6 | 9.1±0.6 | 14.1±3.4 | 15.8±4.0 | 2.3±1.2 | 2.6±1.3 |
| | 5.9 | 6.0 | 9.8±0.7 | 9.0±0.8 | 14.2±3.7 | 15.9±4.0 | 2.3±1.2 | 2.6±1.3 |
| Na-Rb | 7.0 | 9.0 | 9.2±0.6 | 8.5±0.6 | 11.4±3.5 | 12.2±3.5 | 3.4±2.0 | 4.5±2.5 |
| | 5.8 | 7.0 | 9.2±0.4 | 8.6±0.3 | 11.5±1.8 | 12.9±1.9 | 3.4±1.0 | 3.7±1.1 |
| Na-Cs | 6.2 | 7.4 | 9.9±0.4 | 8.9±0.4 | 11.7±1.7 | 13.7±2.0 | 3.7±1.1 | 3.4±1.0 |
| | 5.6 | 6.2 | 9.7±0.5 | 9.2±0.4 | 12.3±1.8 | 14.0±2.2 | 3.1±0.9 | 3.4±1.1 |
| K-Rb | 5.1 | 8.0 | 11.9±0.4 | 11.1±0.5 | 12.2±1.4 | 13.5±1.5 | 3.8±0.9 | 4.4±1.0 |
| | 5.0 | 7.8 | 11.9±0.8 | 11.0±0.8 | 11.7±2.0 | 12.5±2.5 | 4.1±2.0 | 5.0±2.4 |
| | 4.3 | 5.5 | 11.7±0.6 | 10.6±0.6 | 11.5±1.7 | 12.3±1.8 | 4.3±1.3 | 5.1±1.5 |
| K-Cs | 4.8 | 7.5 | 11.9±0.4 | 11.0±0.5 | 12.0±1.6 | 13.0±1.7 | 3.9±1.2 | 4.6±1.2 |
| | 4.3 | 6.1 | 11.9±0.4 | 11.0±0.4 | 11.6±1.5 | 12.4±1.6 | 4.2±1.3 | 5.1±1.3 |
| | 3.5 | 4.6 | 11.3±0.7 | 10.7±0.7 | 12.0±2.3 | 12.7±2.4 | 3.8±1.7 | 4.8±2.0 |

$(d^2V_3/dr^2)|_{r=r_m}$ (the well curvature), since the location of the supernumerary rainbow structure depends more on this quantity than on $r_m$. The locations of the maxima and minima can be fitted equally well with either a 12-6 or an 8-6 potential, and results have been tabulated for both.

The discrepancy between the well depths determined with the two potential models arises from the difference in shape and may be understood from the expression for the classical rainbow angle, Eq. (20). Since $G(12,\ 6)=2.04$ and $G(8,\ 6)=1.84$, we would expect that well depths obtained using a 12-6 model would be about 10% smaller than those obtained with an 8-6 model. The differences observed are of this size and direction within error, indicating that the limit of accuracy in determining the well depth is in the analysis, rather than in the data.

One way of deciding whether the 8-6 or the 12-6 potential model is "better" is to compare the van der Waals constant $C_6$ with the sixth-power term in the LJ potential model. For LJ $n$-6 potentials $C_6 = (n/n-6)\epsilon r_m^6$, so we could easily find which model more nearly agreed with the predictions of theory. We do not feel that this procedure is justified, however, because the rainbow structure is not very sensitive to the long-range "tail" of the potential, and because there is no reason why the actual potential should be accurately represented by a simple LJ potential at all internuclear separations. It does not disturb us, therefore, to find that the values of the sixth-power term in the LJ potentials with parameters determined from Table II generally exceed Dalgarno and Davison's values by a factor of 2–5 (except for Na-K, where the discrepancy is more than a factor of 10).

Our estimates for the triplet well depths in the alkali-alkali systems studied here are all $1.0\pm0.2\times10^{-3}$ a.u. ($4.4\pm0.9\times10^{-14}$ erg). This is roughly twice the value ($2.2\pm0.5\times10^{-14}$ erg) reported by Beck *et al.*[23] for K-Cs. Cowley, Fluendy, and Lawley[24] have reported a value $2.2\pm0.5\times10^{-14}$ erg for Na-K, again roughly $\frac{1}{2}$ of our value. The estimate of Beck *et al.* was obtained by assuming a LJ 8-6 form for the singlet potential and then adjusting the well depth of another 8-6 potential (used to represent the triplet potential) until exact calculations reproduced their differential spin-exchange cross section (they used Buck and Pauly's[19] value of $C_6$ for both potentials). Cowley, Fluendy, and Lawley obtained their estimate by analysis of $\sigma_{\text{sum}}$ for very small angles ($E\theta\leq0.3\times10^{-3}$ a.u.). We feel that both experiments are sensitive to the potentials at large interatomic separations, but that neither one is very sensitive to the depth of the triplet well. Consequently, we view the discrepancy between their results and ours as an indication that a LJ 8-6 potential which is a good fit to the potentials in the asymptotic region will not be good in the rainbow region (and vice versa). We feel that the rainbow position is sensitive primarily to the depth of the well and that our values for $\epsilon$ should be fairly reliable.

## VI. POTENTIALS

In this section we review the current state of knowledge on alkali-alkali potentials, indicating where our results dispute, corroborate, and extend previous knowledge. Our discussion begins at large internuclear separations with the van der Waals interaction and works towards smaller internuclear separations where exchange and core effects become important.

### A. van der Waals Potential

The van der Waals interaction[25] is the strongest interaction between two alkali atoms at internuclear separations between about 10 and $300 a_0$ (beyond $\sim 300 a_0$, the magnetic dipole interaction between the electron spins dominates, although it is too small to produce observable effects in thermal-energy scattering experiments). This interaction is purely electrostatic in origin, and it is consequently independent of the configuration (singlet or triplet) of the electron spins.

The van der Waals interaction has received considerable theoretical attention, and not only the leading term ($C_6 r^{-6}$) but also the inverse eighth- and tenth-power terms have been estimated for the expansion

$$V_w(r) = C_6 r^{-6}[1 + (C_8/C_6) r^{-2} + (C_{10}/C_6) r^{-4} + \cdots]. \quad (22)$$

The van der Waals interaction arises from second-order perturbation theory, and consequently no odd powers of $r$ are involved up to $r^{-11}$, which appears in third order.[26] We feel that the most reliable synthesis of the theoretical results is to use Dalgarno and Davison[18] for $C_6$, Davison[20] for the ratio $C_8/C_6$, and Fontana[21] for the ratio $C_{10}/C_6$. (These are collected in Table III.) Fontana does calculations only for identical pairings; we have used the geometric mean of his ratios to obtain values for the ratios in nonidentical pairs. All of these terms are negative (corresponding to attraction), and the eighth- and tenth-power terms are sizable, ~ 50% of the sixth-power term at $15 a_0$. This is in contrast to most other atomic systems, where the higher-order terms are generally insignificant at distances larger than $10 a_0$.[27]

The van der Waals constant $C_6$ has also been measured by Buck and Pauly,[19] who used a semiclassical treatment to determine $C_6$ from absolute measurements of the total cross section. Their values are generally about 50% of those calculated by Dalgarno and Davison. Smith has suggested[28] that the discrepancy would be resolved if the triplet well depth were very shallow, but our rainbow results, as well as the forward glory measurements of Rothe and Helbing,[29] eliminate this possibility. Buck and Pauly measured the total cross section, which requires absolute knowledge of the target-gas pressure. This is very difficult to measure for condensable corrosive materials like alkali vapors, and it is possible that all of their results could be off by a constant factor. In view of the consistency of the results obtained when they reversed the constituents of the primary beam and target vapor, it seems likely that their relative values of $C_6$ are accurate within about 15%. Dalgarno and Davison's errors in $C_6$ should be roughly 15%; hence, the variation from system to system in the ratio $C_6$ (Buck and Pauly)/$C_6$ (Dalgarno and Davison) appears to be just outside the range permitted by the combined experimental and theoretical errors. (We have assumed that the theoretical errors come only from errors in the oscillator strengths. We have not included the core contribution to $C_6$, since it does not reduce the variation of the ratios. The ratios are listed in Table III.)

Fontana[21] has calculated values of $C_6$ and $C_8$ (in addition to $C_{10}$) for identical alkali-alkali pairings. His results for $C_6$ disagree with Dalgarno and Davi-

TABLE III. Parameters for asymptotic alkali-alkali potentials (in a.u.).

| | $C_6$ | | | | $C_8/C_6$ | | $C_{10}/C_6$ | Parameters for $\Delta V_{DR}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Valence electron | Core | Buck and Pauly | Ratio[a] | Fontana | Davison | Fontana[b] | $N$ | $\gamma$ | $\alpha$ | $b(\tau = 10^{-3})$ |
| Li-Li | 1380 | (9) | | | 46 | 54 | 2581 | $2.28 \times 10^{-3}$ | 3.19 | 1.256 | 13.4 |
| -Na | 1470 | (20) | | | 47 | 57 | 2704 | 1.91 | 3.23 | 1.241 | 13.6 |
| -K | 2240 | (130) | | | 52 | 68 | 3295 | 0.92 | 3.37 | 1.191 | 14.6 |
| -Rb | 2440 | (190) | | | 51 | 71 | 3184 | 0.77 | 3.40 | 1.181 | 14.8 |
| -Cs | 3000 | (280) | | | 54 | 79 | 3608 | 0.54 | 3.47 | 1.161 | 15.3 |
| Na-Na | 1580 | (40) | 920 | 0.58 | 48 | 61 | 2833 | 1.59 | 3.26 | 1.227 | 13.8 |
| K | 2390 | (170) | 1130 | 0.47 | 53 | 75 | 3453 | 0.77 | 3.40 | 1.177 | 14.8 |
| Rb | 2600 | (240) | 1440 | 0.55 | 52 | 79 | 3336 | 0.66 | 3.44 | 1.167 | 15.0 |
| Cs | 3180 | (340) | 1510 | 0.47 | 56 | 82 | 3780 | 0.45 | 3.50 | 1.147 | 15.5 |
| K - K | 3680 | (420) | 1590 | 0.43 | 59 | 86 | 4208 | 0.369 | 3.55 | 1.127 | 15.9 |
| Rb | 4000 | (540) | 1630 | 0.41 | 57 | 89 | 4066 | 0.310 | 3.58 | 1.117 | 16.1 |
| Cs | 4940 | (720) | 1920 | 0.39 | 61 | 93 | 4607 | 0.218 | 3.65 | 1.097 | 16.7 |
| Rb-Rb | 4350 | (680) | 1670 | 0.38 | 57 | 93 | 3929 | 0.260 | 3.62 | 1.106 | 16.3 |
| -Cs | 5370 | (910) | 2150 | 0.40 | 60 | 96 | 4452 | 0.183 | 3.68 | 1.087 | 16.9 |
| Cs-Cs | 6660 | (1180) | 3460 | 0.52 | 64 | 100 | 5044 | 0.128 | 3.75 | 1.067 | 17.5 |

[a] $C_6$ (Buck-Pauly)/$C_6$ (Dalgarno-Davison, no core term).

[b] Geometric mean used for nonidentical pairs.

son, but agree with the results of Buck and Pauly. We regard this agreement as fortuitous: Fontana's hydrogenic wave function approximation does not reproduce the close spacing of the adjacent $p$ state which is a salient feature of alkali atoms, and it is not surprising that it gives lower results than the more realistic model used by Dalgarno and Davison.

While Fontana's results for $C_6$ do not appear to be reliable, his results for the ratios $C_8/C_6$ and $C_{10}/C_6$ are useful. This is partly due to some cancellation of the errors inherent in his model and partly due to the decreased accuracy required in the higher-order terms compared with the leading term. His values for $C_8/C_6$ are compared with Davison's more accurate calculations in Table III, and are typically 30% low (cf. 50% low for his values of $C_6$). This gives us some confidence in his values for the ratio $C_{10}/C_6$, although it would not be surprising if these, too, are somewhat low.

In Sec. IV D we showed that the probability exchange data in I supported the Dalgarno-Davison value of $C_6$ with the inclusion of both eighth- and tenth-inverse power terms in the van der Waals interaction. Our interpretation depends on the DR calculation of the difference potential, but we feel that any revisions of that calculation will require an *increase* in the magnitude of the van der Waals interaction to retain consistency with the exchange data in I. Thus, we feel that the larger value of $C_6$, due to Dalgarno and Davison, is more nearly correct.

### B. Difference Potential

In addition to the theoretical work on the asymptotic expansion coefficients of the van der Waals interaction, there has also been some work on the difference potential,

$$\Delta V(r) \equiv V_3(r) - V_1(r). \tag{23}$$

Dalgarno and Rudge[16] have given an asymptotic expression of the form

$$\Delta V_{\mathrm{DR}}(r) = N r^{2\gamma-1} e^{-a r}, \tag{24a}$$

while Smirnov and Chibisov (SC)[30] have given

$$\Delta V_{\mathrm{SC}}(r) = (J_0 + J_1' r + J_2' r^2) r^{\beta} e^{-\alpha r}, \tag{24b}$$

and Knox and Rudge[17] have found

$$\Delta V_{\mathrm{KR}}(r) = A r^{\beta} e^{a_0/r - \alpha' r}. \tag{24c}$$

The DR calculation is generally the lowest of these, although the SC results lie slightly below $\Delta V_{\mathrm{DR}}$ at large $r$ ($> 20a_0$) in some systems. Generally, $\Delta V_{\mathrm{SC}}$ is 0–30% larger than $\Delta V_{\mathrm{DR}}$. $\Delta V_{\mathrm{KR}}$ is considerably (~80%) larger than $\Delta V_{\mathrm{DR}}$ for all alkali-alkali systems except those which contain Li, in which case $\Delta V_{\mathrm{KR}}$ is between 5% and 60% above $\Delta V_{\mathrm{DR}}$. Some recent calculations by Callaway and Laghos[31] give results about 20–30% greater than $\Delta V_{\mathrm{DR}}$.

In theory, it should be possible to decide among these potentials by measuring the total spin-exchange cross section absolutely by means of optical pumping techniques.[6,32] In practice, this approach has not been very successful, because it is difficult to measure absolute cross sections, and because the cross sections are fairly insensitive to the magnitude of the difference potential and the temperature of the alkali vapor under study. For example, quadrupling the temperature (i.e., doubling the relative velocity) changes the cross section by roughly 8% according to the SC calculations. Since doubling $v_{\mathrm{rel}}$ has roughly the same effect on the phase as halving the difference potential [see Eq. (13)], the cross sections calculated with the largest estimate for the difference potential $\Delta V_{\mathrm{KR}}$ are roughly 8% larger than those calculated with the smallest estimate, $\Delta V_{\mathrm{DR}}$. Recent experimental uncertainties have been between 10% and 20%; hence, these experiments are not decisive in determining which expression for $\Delta V$ is best.

Another difficulty with the use of total cross-section measurements to determine $\Delta V$ lies in the use of the semiclassical approximation. Dalgarno and Rudge[16] estimated that this approximation introduced less than 30% error in the total spin-exchange cross section, an intolerably large amount in view of the precision required to differentiate between various current models for $\Delta V$. Recently, Chang and Walker[33] have tried to eliminate this source of error by doing a complete partial-wave calculation of the total spin-exchange cross section on a computer. This approach requires knowledge of the potentials at all internuclear separations, however, and the potentials which they used are unrealistic and give values for the total exchange cross section which disagree with recent experiments by many standard deviations.

The present work does little to resolve the conflict among the various expressions for $\Delta V$ because the van der Waals potential is not known sufficiently accurately (see Sec. IV D). However, we are able to determine that $\Delta V_{\mathrm{DR}}$ is consistent with our data and the *largest* current estimates for $V_w$, so that a larger $\Delta V$ will be inconsistent with our spin-exchange data, unless $V_w$ is also increased.

This experiment provides some indication that the radial decay factors of the difference potentials in Eq. (24) are about right. This evidence is that the $v\delta(\tau)$ plots (see Figs. 4–8) agree with experiments (or differ by a constant factor) over the range $0.4\times10^{-3} < \tau < 10^{-3}$, where $v\delta$ changes by a factor of roughly 5. This is consistent with the rapidly decaying $\Delta V$'s in Eq. (24), but is inconsistent with $\Delta V$'s which decrease more slowly. As an example, we were unable[34] to fit the experimental data at both ends of this range with $\Delta V = Kr^{-8}$ for any single value of $K$.

All of the theoretical calculations for $\Delta V$ omit consideration of the effects of excited molecular states. We feel that these states may contribute significantly to the difference potential, as suggested by the following semiquantitative argument.

First, neglecting exchange, we calculate the amount of adjacent $p$ states mixed into the wave function for the alkali-alkali system by the long-range electrostatic interaction $V_{\mathrm{el}}$. The wave function is

$$\Psi_{\mathrm{system}} = \Psi_s \Phi_s + \alpha \Psi_p \Phi_p ; \tag{25}$$

$\Psi$ are centered on atom $A$, $\Phi$ on atom $B$, $s$ and $p$ denote the lowest $s$ and $p$ states of each atom. Using first-order perturbation theory we find

$$\begin{aligned} \alpha &= \langle \Psi_s \Phi_s | V_{\mathrm{el}} | \Psi_p \Phi_p \rangle / (E_p^A - E_s^A + E_p^B - E_s^B) \\ &\approx \langle \Psi_s \Phi_s | V_{\mathrm{el}} | \Psi_p \Phi_p \rangle / (2\Delta E), \end{aligned} \tag{26}$$

with $\Delta E \equiv E_p - E_s \approx 0.1$ a.u. for all alkali atoms. It is easiest to evaluate $\alpha$ by noting that the second-order energy is the leading term in the van der Waals interaction:

$$-C_6/r^6 = -|\langle \Psi_s \Phi_s | V_{\mathrm{el}} | \Psi_p \Phi_p \rangle|^2 / 2\Delta E ,$$

so that $\alpha$ (which obviously depends on the internuclear separation $r$ is

$$\alpha(r) = [C_6/(2\Delta E r^6)]^{1/2} . \tag{27}$$

The ambiguity of sign in this expression may be resolved by using Eq. (26) and an explicit expression for $V_{\mathrm{el}}$. At $\tau = 10^{-3}$ in Na-Cs, $b = 15.5 a_0$ and $C_6/r^6 \approx 2 \times 10^{-4}$ a.u., so that $\alpha \approx 0.03$.

This may seem negligible, but it can have a considerable effect on $\Delta V$, which is roughly proportional to the square[35] of the overlap integral,

$$\begin{aligned} S &= \langle \Psi_{\mathrm{system}} | P | \Psi_{\mathrm{system}} \rangle = \langle \Psi_s | \Phi_s \rangle \langle \Phi_s | \Psi_s \rangle \\ &\approx |\langle \Psi_s | \Phi_s \rangle|^2 + 2\alpha |\langle \Psi_s | \Phi_p \rangle|^2 + \mathcal{O}(\alpha^2), \\ &+ 2\alpha \langle \Psi_s | \Phi_p \rangle \langle \Psi_p | \Phi_s \rangle + \alpha^2 \langle \Psi_p | \Phi_p \rangle \langle \Phi_p | \Psi_p \rangle \end{aligned} \tag{28}$$

(in the last step we assume that the alkalis are identical to achieve greater simplification). Since $\Psi_p$ is roughly three times as large as $\Psi_s$ at distances of $7-9 a_0$ (i.e., midway between the atoms), it is reasonable to suppose that $|\langle \Psi_s | \Phi_p \rangle|^2$ is roughly ten times as large as $|\langle \Psi_s | \Phi_s \rangle|^2$. Hence, we have

$$\Delta V \sim S^2 \approx (1 + 40\alpha) |\langle \Psi_s | \Phi_s \rangle|^2 . \tag{29}$$

Obviously, a value of $\alpha$ as small as 0.01 could still affect $\Delta V$ quite significantly!

This discussion has neglected the fact that there are three $p$ states for each atom and that $\Delta V$ mixes in each possible intermediate state with its own value of $\alpha$, and it also neglects spin-orbit coupling. Nevertheless, we believe that it shows the need for calculations of $\Delta V$ which include some excited intermediate states.

### C. Asymptotic Form for Potentials

Both the van der Waals potential [Eq. (22)] and the difference potential [Eq. (24)] are asymptotic expressions, valid as $r$ increases to large values. These may be combined to find an asymptotic form for the singlet and triplet potentials according to the relationship

$$V_3(A) = V_w(r) + \tfrac{1}{2}\Delta V(r) , \tag{30a}$$

$$V_1(r) = V_w(r) - \tfrac{1}{2}\Delta V(r) . \tag{30b}$$

The assumption underlying Eq. (30), namely, that $V_w(r)$ lies midway between $V_1$ and $V_3$, may be questioned[36] because it ignores the electrostatic effects of electron-cloud overlap. (The van der Waals interaction is calculated from the power series for nonoverlapping charge distributions.) These effects are small between spherical electron clouds with exponentially decaying charge densities (like alkali-valence electrons), because the electrostatic potential inside such a charge density is nearly equal to the potential generated by a point charge of magnitude $-e$ placed at the nucleus. This may be seen by considering the potential at a point a distance $R$ from the center of such a charge distribution: Charge with $r \leq R$ acts as if it were at the origin, while the charge density with $r > R$ is decaying exponentially and contributes to the potential roughly $R/(R+d)$ as much as if it were at the origin. Here $d$ is the decay length for the charge distribution, typically $d \lesssim a_0$ for alkali-valence electrons. In the region of maximum overlap $R \approx 7$, so $R/(R+d) \approx 0.9$. A more detailed discussion of the effects of charge overlap has been given by Kreek and Meath.[37]

The burden of this argument is that the effects of electron-cloud overlap are small for internuclear separations larger than $10 a_0$ or so, so that Eq. (30) should be a good representation of the asymptotic behavior of the potentials. Further evidence to this effect is given by Kolos and Wolniwiecz,[38] who showed that, for the system H-H, the van der Waals energy [including terms through $C_{10} r^{-10}$ in Eq. (22)] equals the average energy $\frac{1}{2}[V_1(r) + V_3(r)]$ within 5% for $r \geq 8.0 a_0$. [The minimum in $V_3(r)$ occurs at $r = 7.85 a_0$ in the H-H system.]

### D. Potential Minima

The singlet potential in alkali-alkali systems have deep minima whose well depths may be obtained from spectroscopic data for the corresponding bound molecular states.[11] Typical depths range from $\frac{1}{2} \rightarrow 1$ eV($\sim 0.03$ a.u.) with $r_m \approx 6 a_0$. In addition, forward glory measurements of alkali-alkali systems at high energies[22] provide a measure of the product $\epsilon r_m$ for the singlet potential well. The singlet well shape, as determined mainly by analysis of spectroscopic data, has been "patched on" to the van der Waals potential by Vietzke and Schlier[39] to form an estimate for the singlet potential in Na-Cs. We feel that this is a reasonable procedure for obtaining an approximate singlet potential, although we feel that our asymptotic expression for the singlet potential [Eq. (30)] is more reliable than the one which they used, since they omitted the $-C_{10}r^{-10}$ and $-\frac{1}{2}\Delta V$ terms.

The triplet potential minimum lies at moderate internuclear separations ($\sim 10a_0$), and has a depth of about $10^{-3}$ a.u. (about $\frac{1}{30}$ of the singlet well depth). The present experiments and those by Rothe and Helbing[29] provide, in our opinion, the only reliable information on the minimum of the triplet potential. The only theoretical estimates of the well depth have been based on Eq. (30), which does not yield a minimum for $V_3$ if the eighth and tenth inverse powers of $r$ are included in the van der Waals interaction [Eq. (22)]. When these terms are omitted, one obtains a shallow well about $10^{-5}$ a.u. deep,[28] much too small to explain the structure in $\sigma_{\text{sum}}$ which we attribute to the triplet scattering.

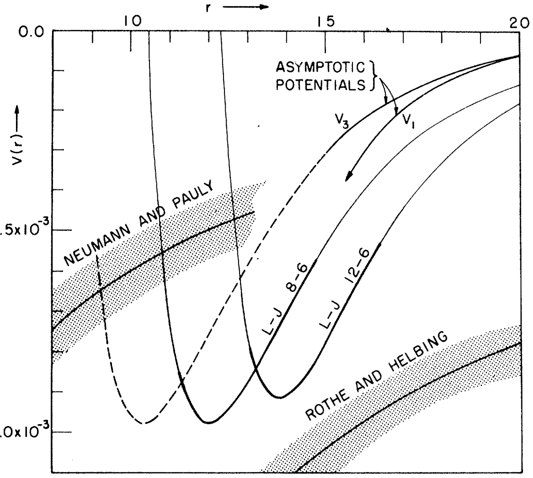

FIG. 10. 12-6 and 8-6 potentials which fit our data for Na-Cs (a heavy line is used for the region most sensitive to the data). The asymptotic potential is extended (dashed line) by translating the 8-6 minimum to join it at $15a_0$. The location of the minimum found in this manner is inconsistent with both previous forward glory measurements (shaded bands).

### E. Conclusion – The Triplet Potential in Na-Cs

Schlier and Vietzke's technique of fitting the shape of the singlet minimum together with the asymptotic potential should result in a potential which is consistent with both our exchange data and the other data on the singlet minimum.[11,22] Let us now investigate the possibility of using a similar technique for the triplet potential.

For the triplet potential, we desire to connect the asymptotic potential [Eq. (30)] smoothly onto a potential minimum with the characteristics found from our analysis of the rainbow data (Sec. V). Figure 10 shows both the 8-6 and 12-6 potential minima found from the rainbow analysis for Na-Cs, along with the asymptotic potentials.

The rainbow structure is determined principally by the behavior of the potential near its minimum, and, consequently, these fits are best in that vicinity (this region is drawn with a heavy line in Fig. 10). Note that the shapes of the two fits are practically identical, and that the well depths differ by only a few percent. The locations of the two wells differ, but this is to be expected for determinations based on rainbow structure (see Sec. V). Thus, we would expect that a potential composed of the asymptotic potential for $r > 15a_0$ with a minimum whose shape was that of either the 12-6 or 8-6 minimum (for $r \leq 15$) would reproduce the rainbow structure. We have suggested such an approach previously,[40] and the appropriate extension of the asymptotic potential is shown dashed in Fig. 10. Note that the slopes of the two pieces of the potential are nearly equal at $r = 15a_0$. This indicates that our grafting operation may have produced a reasonable potential.

We have chosen to illustrate the Na-Cs system in Fig. 10 because there are two measurements of the oscillations in the total cross section with changing energy for this system.[22,29] This type of measurement accurately determines the quantity $a\epsilon r_m$, where $a$ depends on the shape of the potential. [$a$ lies between 0.4 and 0.5 for LJ ($n$-6) potentials with $n$ from 7 to 15.] Taking $a = 0.45 \pm 0.05$, we find $(\epsilon r_m)_{\text{triplet}} = 6.0 \pm 1.2 \times 10^{-3}$ from Neumann and Pauly's data,[22] while $(\epsilon r_m)_{\text{triplet}} = 15.6 \pm 1.5 \times 10^{-3}$ from Rothe and Helbing's data[29] (both for the triplet potential in a.u.). Recently Neumann and Pauly[41] have confirmed the value of a $\epsilon r_m$ determined by Rothe and Helbing. The corresponding hyperbola (see Fig. 10) passes well below the minimum of our grafted potential (for which $\epsilon r_m \approx 10^{-3}$ a.u.).

This discrepancy is not a consequence of our grafting procedure – it stems from an incompatibility of the analysis of the experimental data with the asymptotic potential. Taking $\epsilon$ from the rainbow data and $\epsilon r_m$ from the glory data gives $r_m \approx 16a_0$, which is incompatible with the asymptotic potential, or any revision of it compatible with our $v\delta(\tau)$ analysis. [If the DR difference potential were a factor of 4 too small, for example, agreement with the experimental $v\delta(\tau)$ results could be regained if $C_6$ were increased by a factor of roughly 2. This would lower the asymptotic triplet potential by less than a factor of 2, and it would still be incompatible with a potential minimum at $16a_0$.]

Thus, our interpretation of the data in I deepens the problems associated with the triplet Na-Cs potential. While it may be possible to find a potential which will be consistent with all the data, it appears more difficult to do this here than in the alkali-noble-gas systems (where it has been done[42]) due to the large magnitude of the discrepancies. Measurements of the differential cross section with increased resolution (so that the rapid oscillations could be observed) would be quite valuable, as would theoretical calculations of the potential shape near the minimum.

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