

Interatomic potentials from velocity-changing collision kernels

K. E. Gibble* and J. Cooper

Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology,
Boulder, Colorado 80309-0440

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Measurements of velocity-changing collision kernels have recently been reported. Here we describe the results of calculations which demonstrate that interatomic potentials can accurately be derived from such data. It is important to analyze the kernel directly in terms of an interatomic potential and not in terms of a traditional energy-averaged differential cross section. We use experimental results to determine the Rb-He potential and compare it to calculated potentials.

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Much detailed information about interatomic potentials has been obtained from atomic- and molecular-beam scattering experiments. These experiments usually involve a very complicated and costly apparatus and are often difficult due to small signals. In contrast, a one-dimensional velocity-changing collision (VCC) kernel can be measured with a relatively simple apparatus—two narrow-band diode lasers and a cell containing active atoms and a buffer gas [1]. The one-dimensional VCC kernel $W(v_z' \rightarrow v_z)$ is the probability density per unit time that an active atom's initial velocity component v_z' is changed to v_z due to a collision with a buffer gas atom. These initial and final velocity components are selected, due to the Doppler shift, by the laser detunings so that the component of the experimental signal related to a single VCC is

$$S_1(v_z, v_z') = \int_{-\infty}^{\infty} dv_z'' \int_{-\infty}^{\infty} dv_z^{(3)} n(v_z') P(v_z'' | v_z') \times W(v_z'' \rightarrow v_z^{(3)}) P'(v_z^{(3)} | v_z). \quad (1)$$

Here $n(v_z)$ is the density of ground-state atoms and P and P' are the pump and probe laser atomic-excitation func-

tions which are often Lorentzians. Measurements versus buffer gas pressure enable the extraction of the signal S_1 without the effects of atoms which undergo no collisions [$W(v_z' \rightarrow v_z)$ replaced with $\delta(v_z - v_z')$ in Eq. (1)] or atoms which have two or more collisions [1]. In a cell with initially thermal velocity distributions, the transverse velocity of the active atom and the speed and direction of the perturber are random. Unlike beam experiments, these random velocities lead to randomly oriented collision axes and a thermal distribution of collision energies. Previously, Gorlicki, Lermينياux, and Dumont have shown that theoretical potentials can be used to reproduce saturated absorption line shapes obtained in buffer gas cells [2]. More recently, Keller and Le Gouët have used stimulated photon echos to extract van der Waals coefficients from measured VCC cross sections [3]. Here we show that VCC kernels can be used to determine a model-independent interatomic potential and, in light of all of the thermal averages, an incredible sensitivity of the kernel to the interatomic potential is shown.

The VCC kernel can be calculated from the differential cross section $d\sigma/d\Omega$ as a function of the center-of-mass scattering angle θ and the relative speed v_r of the active atom and perturber [4]:

$$W(v_z' \rightarrow v_z) = N \left(\frac{m_a}{\mu} \right)^3 \int d\mathbf{v}'_{tr} \int d\mathbf{v}_{tr} \int d\mathbf{v}'_p \int d\mathbf{v}_p W(v'_{tr}) W_p(\mathbf{v}'_p) \delta \left(\mathbf{v}'_p - \mathbf{v}_p + \frac{m_a}{m_p} (\mathbf{v}' - \mathbf{v}) \right) v_r^{-1} \delta(v_r - v_r') \frac{d\sigma(\theta, v_r')}{d\Omega}, \quad (2)$$

$$\theta = 2 \sin^{-1} \frac{|\mathbf{v} - \mathbf{v}'|}{2v_r'}$$

Here the δ functions represent momentum and energy conservation, $W_p(\mathbf{v}'_p)$ and $W(v'_{tr})$ are the initial thermal perturber and active atom transverse velocity distributions where $\mathbf{v}' = \mathbf{v}'_{tr} + v_z' \hat{z}$, $\mathbf{v}'_r = \mathbf{v}' - \mathbf{v}'_p$ and \mathbf{v}_r are the relative velocity vectors, and N is the buffer gas density.

In this work, we have instead chosen to perform a Monte Carlo simulation to calculate the kernel which facilitates the calculation of correlations between velocity changes and other variables. The active atom's transverse velocity and the three components of the perturber's velocity are randomly chosen from thermal distributions. In addition, an impact parameter b and the azimuthal

scattering angle ϕ are chosen. Here we consider collisions between two spherically symmetric atoms and therefore, the scattering is azimuthally symmetric about the collision axis. However, due to the random collision axes orientations, we must randomly choose ϕ , since the laboratory-frame velocity depends on ϕ . From these "initial conditions," the final velocity v_z is classically uniquely determined. Thus, the "bin" into which v_z falls is incremented by a weight. If a uniform distribution of impact parameters b is chosen, this weight is $2\pi b b_{\max} v_r$ [5]. The v_r factor represents the higher collision frequency for atom pairs with large relative velocities and the b_{\max} is chosen

sufficiently large such that essentially no collisions at larger b 's produce velocity changes larger than half of the bin width. The kernel calculated using this simulation technique is equivalent to the integrals of Eq. (2) [5]. Calculations of kernels by Ho and Chu [4] and an uncertainty principle argument by Berman, Mossberg, and Hartmann [6] imply that a classical scattering treatment is appropriate for $|v_z - v_z'| \gtrsim 5 \text{ ms}^{-1}$ for many atom-atom systems near 300 K.

To illustrate the qualitative dependence of VCC kernels on the interatomic potential, in Fig. 1 we show several model potentials and corresponding kernels for $v_z' = 1.37u_a$ and $m_p = m_a$ where $u_a^2 = 2kT/m_a$ (and $N=1$). (The mean collision energy E_c for a thermal gas is 2 kT.) The kernels in Fig. 1(b) rise rapidly at small velocity changes, which is a general feature caused by the large "cross section" of the weak long-range portion of interatomic potentials. The kernel for $v_z' \neq 0$ is not symmetric since the active atoms are colliding with perturbers which are, on average, at rest. Therefore, it is rare that a perturber "catches up from behind" and produces a much larger v_z of the active atom. The shallow potential [dashed line in Fig. 1(a)] produces smaller angle scattering and hence smaller velocity changes at b values corresponding to trajectories through the potential minimum. This is evident in Fig. 1(b) as the shallow potential produces fewer velocity changes near $v_z = 0.7u_a$ and more near $v_z = 1.2u_a$. In addition, the kernel is sensitive to the slope of the repulsive core of the interatomic potential from a comparison of the solid and dotted kernels in Fig. 1(b). Naturally, there is $\approx 50\%$ difference in cross section, but, more interestingly, the "slopes" of the kernels in the semilogarithmic plot are also different between $v_z = 1$ and $-0.5u_a$; the kernel corresponding to the softer (dotted line) potential is actually larger near $v_z = 0.8u_a$. This difference in slope is due to the increased backscattering for the harder (solid line) potential in Fig. 1(a).

To illustrate the dependence of the kernel on the mass ratio and initial velocity, in Fig. 1(c) we show kernels for the solid potential for several mass ratios m_p/m_a and $v_z' = 1.37u_a$ and $m_p = m_a$ and $v_z' = 0$. The kernel for $v_z' = 0$ is symmetric about $v_z = 0$ and has features similar to the $v_z' = 1.37u_a$ kernel. Since heavier perturbers can transfer more momentum per collision, the large velocity-change portion of the kernel is broader for $m_p/m_a = 10$ vs 0.1. In addition, since the collision frequency $\Gamma_c = \int W(v_z' \rightarrow v_z) dv_z = N v_r \sigma$ is not very different for $m_p = m_a$ vs $m_p = 0.1m_a$, the kernel for $m_p = 0.1$ is broader at small velocity changes than that for the heavier perturbers.

Historically, scattering experiments have been analyzed in terms of an energy averaged $d\sigma/d\Omega$ [7]. In this spirit, we have calculated the average center-of-mass scattering angle $\langle \theta(v_z; v_z') \rangle$, where θ has been averaged over all collisions which change v_z' to v_z for several values of m_p/m_a and v_z' . To determine the range of angles corresponding to a particular v_z , we also have calculated the variance σ_θ and we identify $2\sigma_\theta$ as the scattering-angle resolution. The results were found to be relatively insensitive to the potential. In this manner we find that due to the range of angles contributing to a given change in velocity, an energy-averaged $d\sigma/d\Omega$ can be determined uniquely at

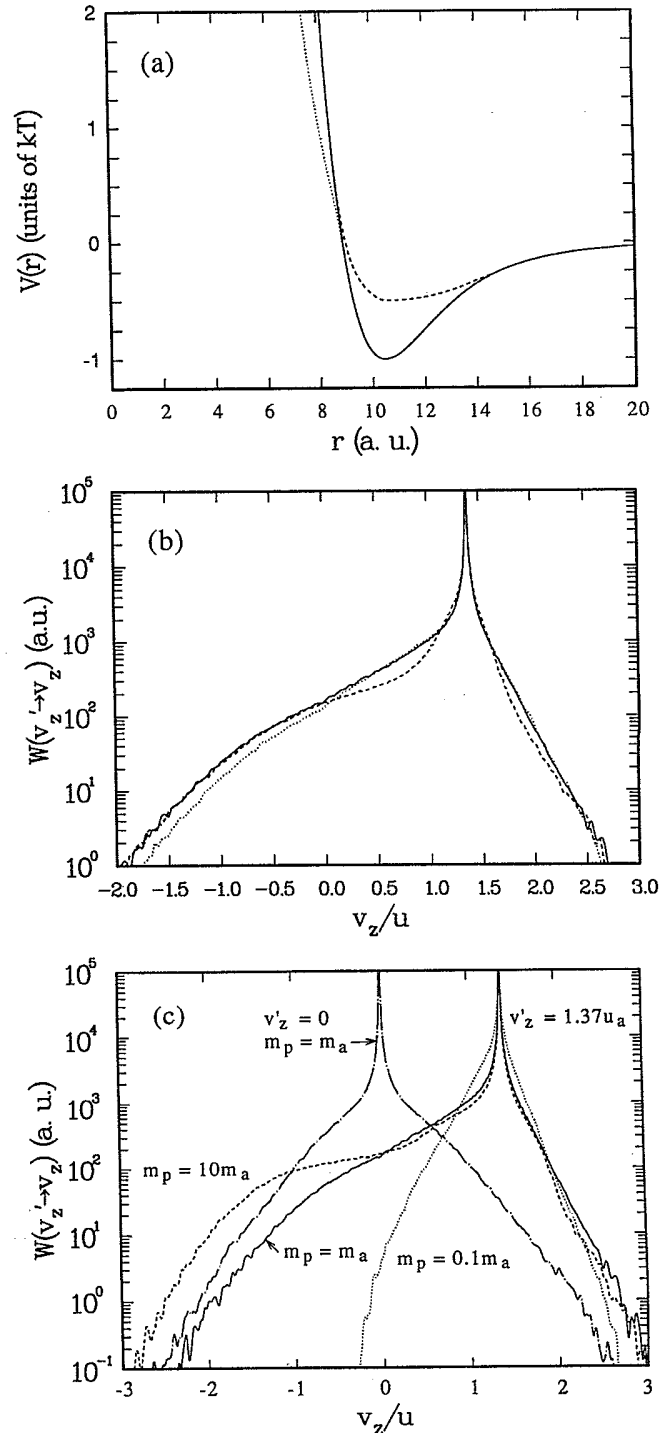


FIG. 1. (a) Model potentials and (b) corresponding kernels for $m_p = m_a$ and $v_z' = 1.37u_a$. (c) Kernels for the solid model potential for $m_p = m_a$ and $v_z' = 0$, and $v_z' = 1.37u_a$ and $m_p/m_a = 0.1, 1, \text{ and } 10$. The "noise" in (b) and (c) illustrates the statistical uncertainty in the calculations.

only ≈ 2 ranges of scattering angles for $m_p \lesssim 10$ and $v_z' \lesssim u_a$. The angular resolution decreases as $v_z' \rightarrow 0$ due to the increasing importance of the random transverse velocity and as $m_p \rightarrow 0$, the collision axes become more isotropic which also decreases the resolution. For $v_z' \rightarrow \infty$ and

$m_p \rightarrow \infty$, each v_z uniquely corresponds to a particular θ [8]. However, in practice v_z' must be less than $\approx 3u_a$ due to the Lorentzian wing excitation of atoms with $|v_z'| \lesssim u_a$ and thus the resolution is limited to $\approx 30^\circ$ [9].

From the above argument, one concludes that the interatomic potential cannot be determined accurately when the kernel is analyzed in terms of an energy-averaged $d\sigma/d\Omega$. However, θ is strongly correlated with the collision energy and this correlation preserves, despite all of the averages, the resolution of the interatomic potential; i.e., a larger collision energy implies a smaller θ (for the same impact parameter), but the velocity change is often nearly conserved. Since most of the deflection usually occurs at the turning point r_0 in the classical trajectory (i.e., distance of closest approach) the resolution of the potential contained in $W(v_z \rightarrow v_z')$ is very nearly the variance of the turning points for all of the collisions. Therefore in Fig. 2 we show the turning point, again averaged over all collisions that change v_z' to v_z , and $\langle r_0 \rangle \pm \sigma_r$ for several v_z' and m_p using the solid potential of Fig. 1(a). In Fig. 2 the variance σ_r , or uncertainty in r_0 increases dramatically at velocity changes that correspond to trajectories passing through the potential minimum ($r_0 \approx 10a_0$). This is expected since, at the potential minimum, there is no relative force between the atoms and, hence, no strong selectivity in the turning point versus θ or velocity change. Surprisingly, in contrast to the case of $d\sigma/d\Omega$, we see in Fig. 2 that the resolution of the potential is relatively independent of m_p/m_a . For $v_z' > u_a$ the kernels contain more information about backscattering (and hence the repulsive core), since for $v_z' \approx 0$ the backscattering is masked by the abundance of small-angle scattering [1].

Using the results of Fig. 2, one can determine the interatomic potential. First, an interatomic potential is arbitrarily specified at ~ 5 internuclear separations. The kernel, $\langle r_0(v_z; v_z') \rangle$, and $\sigma_r(v_z; v_z')$ are then calculated. Now knowing a range of v_z , (v_1, v_2) , which corresponds to a range of $r_0 dr_0 = 2r_0 \sigma_r$, the potential can be iteratively adjusted in the following way. Since $\int_{v_1}^{v_2} W(v_z' \rightarrow v_z) dv_z \propto d\sigma/d\Omega \propto b db$ and since $b = r_0 [1 - V(r_0)/E_c]^{1/2}$, we get

$$\int_{v_1}^{v_2} W(v_z' \rightarrow v_z) dv_z \propto r_0 dr_0 \left[1 - \frac{V(r_0)}{E_c} \right] - \frac{r_0^2}{2E_c} \frac{dV(r_0)}{dr} dr_0. \quad (3)$$

Thus, for small θ , $V(r_0) \ll E_c$ and $dV(r_0)/dr \ll E_c/r_0$ and so $b db \approx r_0 dr_0$. Similarly, for large θ , we get $b db \approx -(r_0^2/2E_c)(dV/dr)dr_0$. Therefore, one increases the kernel in the region of small velocity changes ($v_1, v_2 \ll u_a$) by increasing the range of $V(r)$. For large velocity changes ($v_1, v_2 \approx u_a$), the kernel is increased by increasing the steepness of $V(r)$.

In Fig. 3 we show our fitted Rb-He potential two theoretical potentials, the corresponding VCC kernels, and the reduced data from Ref. [1] for 1 mTorr of He. Here the kernels have been integrated over a $\Delta v_z \approx 1.25$

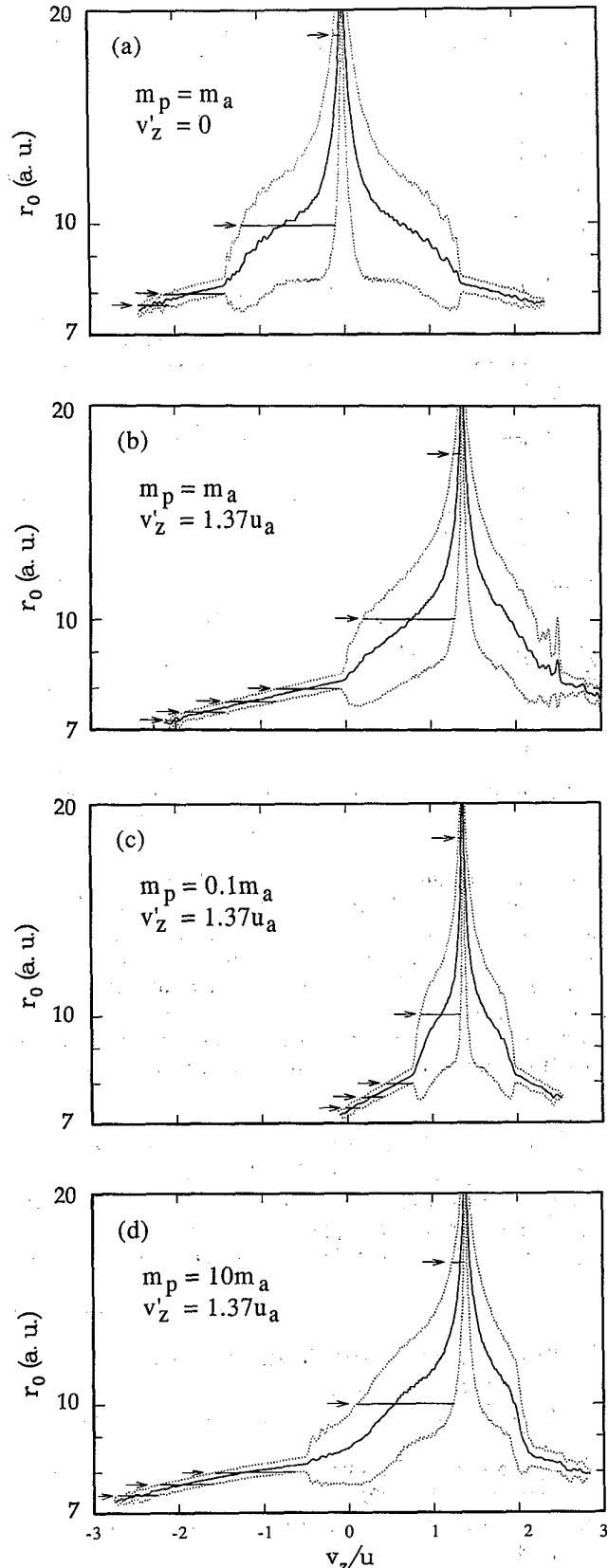


FIG. 2. Average turning point $\langle r_0 \rangle$ (solid lines) and $\langle r_0 \rangle \pm \sigma_r$ (dotted lines) for the kernels of Fig. 1(c). Line segments with arrows denote r_0 's which correspond directly to ranges of v_z and, thus, the internuclear separations where the potential can be determined.

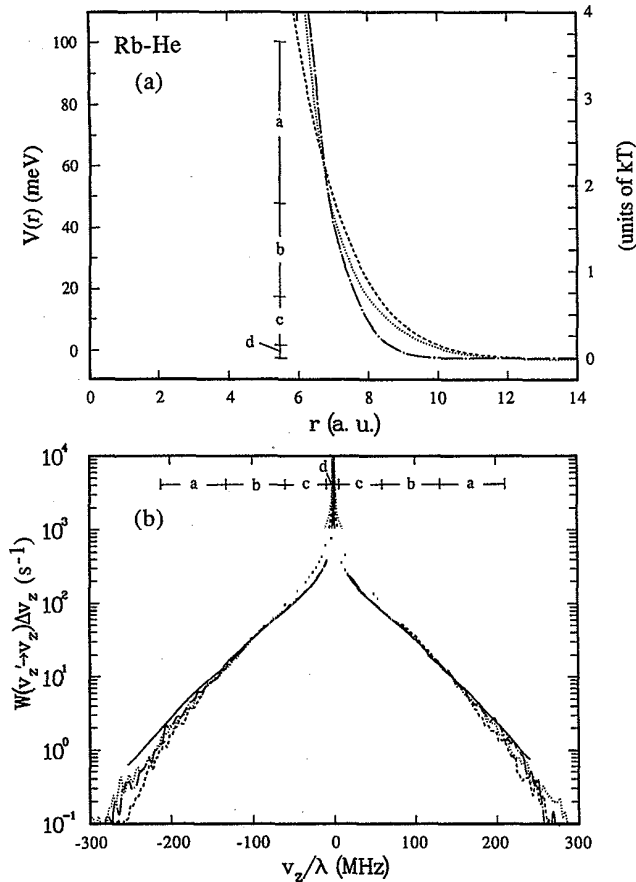


FIG. 3. (a) Rb-He interatomic potentials; dashed-dotted curve: potential derived from experimental data of Ref. [1]; the dashed and dotted curves: calculated potentials of Refs. [10,11] where the radial scale of Ref. [10] has been expanded by 21%. (b) Experimental Rb-He data of Ref. [1] (solid) and kernels calculated from the potentials of (a). Here $T=313$ K, $u_a/\lambda=306$ MHz ($\lambda=795$ nm), and the potential energy ranges $a-d$ of the potentials in (a) correspond to the ranges of v_z in (b).

m/s bandwidth which corresponds to the 1-MHz probe-laser frequency steps used in Ref. [1]. Since the absolute magnitude of the experimental kernels is somewhat uncertain, we have chosen to expand the radial scale of the potential of Ref. [9] by 21% for the sake of comparison, i.e.,

thereby increasing the absolute magnitude of the kernel by 46%. In the experiment, the transverse velocity distribution was slightly subthermal due to the optical pumping technique [1]. Although this does not produce dramatic changes ($\lesssim 15\%$), this velocity distribution was used in these calculations [5].

Using a linear extrapolation between the points specified on $V(r)$, we find that ≈ 12 points, rather than 5 as suggested by Fig. 2(c), are required to reproduce the data to within 5%. In Fig. 3 we have specified 10 points on $V(r)$ and used a cubic spline interpolation in order to produce a smoother, and more realistic, $V(r)$ and $W(v_z' \rightarrow v_z)$. As expected from Fig. 3(b), the calculated potentials of Pascale and Vandeplanque [10] and of Pascale [11] have a much longer range interaction than the potential we determine from the experimental data. The energy ranges $a-d$ of the potential and the corresponding ranges of v_z in Fig. 3(a) and 3(b) elucidates the significance of the differences between the various potentials [see Eq. (3)]. The Rb-He kernel was measured for $v_z'/u_a \approx 0$ and for $v_z'=1.37u_a$. The potential in Fig. 3(a) was fit to their $v_z'/u_a \approx 0$ data [Fig. 3(b)] and also reproduced their $v_z'=1.37u_a$ data. We note that due to the optical pumping technique of Ref. [1], their data strictly represent the VCC kernel only if the transverse velocity of the Rb atom is unchanged by a VCC [1], a good approximation for Rb-He. For heavier perturbers, which can cause the Rb atoms to reenter the laser beam after undergoing a VCC outside the laser beam volume, this is not a good approximation. For this reason, kernels entirely consistent with their data could not be obtained for the heavier perturbers [5]. Further calculations that model this effect or a "pulsed-laser" experimental technique [5] should eliminate these discrepancies.

We have demonstrated that a simple apparatus that produces relatively large signals can be used to determine interatomic potentials. Despite all the random thermal velocities present in a VCC kernel, the potential can be determined if the data are analyzed directly in terms of the potential.

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*Present address: Physics Department, Stanford University, Stanford, CA 94305-4060.

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