"Eclipse" Effect in the Scattering of Weakly Bound Helium Clusters

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The total cross sections of the helium dimer, trimer, and tetramer for scattering from Kr atoms have been measured for cluster beam velocities between 250 and 820 m/s. The dimer cross section is twice that of the atom within 5% indicating that the Kr atoms scatter from the He atoms independently, which is consistent with the large dimer bond distance of about 50 Å. The trimer and tetramer cross sections are somewhat larger and can be described by an impulse approximation with a multiple "eclipse" correction, extending ideas of Glauber for high energy collisions with the deuteron.

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^{4}He exhibits a wide range of unique phenomena, notably superfluidity, not shared by any of the other elements, which result ultimately from its Boson character, a light mass, and very weak interaction potential. Thus small ^{4}He clusters have very large average interparticle distances and are the most tenuous and quantum delocalized of all known complexes. The interatomic potential could be calculated only rather recently with sufficient accuracy to predict the existence of a weakly bound dimer in a single s state [1,2]. Unequivocal experimental evidence for the existence of the dimer was first provided in 1994 by diffracting a molecular beam of small He clusters from a nanostructured transmission grating [3]. Subsequently the average dimer bond distance could be determined from the relative diffraction intensities out to the 7th order to be $\langle r_{ij}\rangle = 52 \pm 4$ Å [4] making it the largest of all naturally occurring ground state diatomic molecules. The large bond distance compared to the effective range of the potential ($r \approx 7$ Å) indicates a very extended halo and facilitates the determination of the binding energy of $E_b = 1.3 \times 10^{-3}$ K from the magnitude of $\langle r_{ij}\rangle$ [4]. The halo of the dimer is closely analogous to that of the deuteron, taking into account that the potential range, bond distance, and scattering length of the dimer are all about a factor 10^6 greater, whereas its binding energy is a factor 10^{13} smaller [5]. The ^{4}He trimer is also unusual since it is a candidate for a special type of very diffuse quantum-mechanically bound state called an Efimov state [6] with $\langle r_{ij}\rangle \approx 80$ Å (see Table I) as predicted by a large number of calculations [10,11]. Its presence, however, has not been demonstrated so far. The somewhat more tightly bound tetramer probably also has only one extended excited state [7]. Their great degree of quantum delocalization explains why these fragile clusters have a single collective excited state, whereas a solid van der Waals cluster with N atoms would have an abundance of states associated with the $3N - 3$ degrees of freedom. Table I summarizes theoretical predictions for these small clusters and compares them with the atom and bulk properties.

The present scattering experiments were undertaken to further explore the structures of these unusual clusters, which except for the dimer up to now have only been simulated using quantum many-body theory [7,8]. In fact, the diffraction experiments used previously to determine the dimer size [4], and here to size select the clusters, may be described in terms of the scattering from the relatively large 50 nm bars of the transmission gratings [12]. Thus complementary information is expected by scattering these clusters from atoms which are smaller or comparable in size.

The He dimer cross section measured in these experiments is almost exactly twice the atom cross section indicating that the Kr atoms are scattered independently from one or the other of the He atoms. This result differs from earlier experiments for the scattering of the heavier rare gas dimers Ne_2, Ar_2, Kr_2 from other heavy rare gas atoms [13]. These dimer cross sections were less than a

TABLE I. Some theoretically predicted properties of small ^{4}He clusters.

Species	J[a]	E_i [mK][b]	$\frac{\langle T\rangle}{N}$ [K][c]	$\langle r_{ij}\rangle$ [Å][d]	$\langle r_{ij}^{-2}\rangle$ [Å^{-2}][e]
He_2	0	1.3[f]	0.05	52[f]	0.0048
He_3					
Ground	0	125	0.58	9.56	0.0233
Efimov	0	2.19	...	80[g]	...
He_4					
Ground	0	560	0.90	7.70	0.0251
Excited	0	133	...	...	...
Bulk	...	7.15 K[h]	13.5	3.6	...

[a] J is the angular momentum quantum number.
[b] E_i is the binding energy .
[c] $\langle T\rangle/N$ is the average kinetic energy per atom .
[d] $\langle r_{ij}\rangle$ is the average interparticle spacing .
[e] The averaging was calculated using wave functions reported in Ref. [9].
[f] Ref. [4].
[g] Ref. [10].
[h] The heat of evaporation.

factor 1.5 (Ne_2) and typically factor a 1.3 larger than the corresponding atom-atom cross sections, which could be explained by the well known pairwise additive potential model. Not only does this approach not work for the He dimer, but it also does not apply to the trimer and tetramer cross sections, which would be predicted to be at most a factor of 1.6 and 1.7 larger, respectively, instead of a factor of 2.5 and 3.0 as found here. A satisfactory explanation of the present cross sections is provided only by an approximation in which the overall cross section is the sum of the atom-atom cross sections, with a correction for shadowing in eclipse positions [14,15].

The clusters are produced in a free jet cryogenic expansion of the pure ^{4}He gas through a 5 μm diameter orifice at source pressures between $P_0 = 0.8$ and 140 bars for source temperatures between $T_0 = 6$ and 60 K, respectively, and have velocities between 250 and 820 m/s. The atom de Broglie wavelengths range from 4.0 to 1.2 Å and the clusters have smaller de Broglie wavelengths corresponding to their larger masses. At optimal conditions the mole fractions of clusters in the beam are about 7% (He_2), 6% (He_3), and 1% (He_4) [16]. These clusters have the same mean laboratory velocities as the atoms to within 1% and very narrow velocity distributions with a FWHM of about $\Delta v/v \approx 1\%$ and therefore large longitudinal coherence lengths of 100–400 Å [17]. Figure 1 indicates the beam defining dimensions of the apparatus [18]. The narrow 20 μm $\times$ 5 mm slits provide both for the high angular resolution required for resolving the cluster peaks and for measuring the quantum mechanical total integral cross sections. The liquid nitrogen cooled ($T = 77$ K) scattering cell with 0.5 mm $\times$ 5 mm slits at both ends provides for a 5.0 cm long scattering path. Kr gas was chosen as a target since the He-Kr van der Waals potential is well known [19] and its average velocity at 77 K is $\langle v \rangle = 139$ m/s and less than even the lowest primary beam velocity of 250 m/s.

Figure 2 shows a typical diffraction pattern for $v = 415$ m/s at $T_0 = 17$ K, $P_0 = 7$ bars (inset) and a typical measurement of the attenuation of the specular peak and of the first order diffraction peak intensities of the He atoms, He_2, He_3, and He_4 clusters.

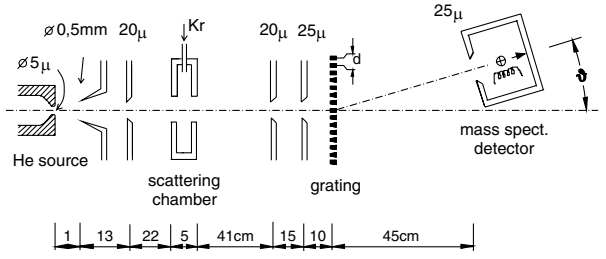

FIG. 1. Schematic diagram of the apparatus showing the important dimensions which determine the angular resolution. The entire apparatus is divided up into eight different pumping stages to reduce the background in the mass spectrometer detector chamber.

Figure 3(a) displays the velocity dependence of the He-Kr total integral cross sections σ_{at} obtained from attenuation measurements via Beer's law $I_{at} = I_{at,0} \times \exp(-\sigma_{at} n l)$, where n and l are the scattering gas density and scattering length and the index "at" denotes the atom. The index 0 refers to measurements without scattering gas. Corrections to the cross section to account for the finite angular resolution of 70 μrad FWHM are estimated to amount to $\Delta\sigma/\sigma < 1\%$ [20] and, consequently, could be neglected. To avoid the difficult task of measuring absolute cross sections [20] the ratios of the cluster cross sections relative to the He-Kr cross section were determined by comparing cluster peak intensities to the atom peak intensity using the simple relation

$$\frac{\sigma_{cl}}{\sigma_{at}} = \frac{\ln(I_{cl}/I_{cl,0})}{\ln(I_{at}/I_{at,0})}, \tag{1}$$

where the index "cl" denotes the cluster. In Figs. 3(b)–3(d) these ratios are plotted as functions of the beam velocity.

The halo in the dimer and other analogies to the deuteron suggest that the impulse approximation with multiple scattering corrections introduced by Glauber [14] can be used to explain these experiments. This elegant theory is based on the following assumptions: the de Broglie wavelength of the colliding particles in the

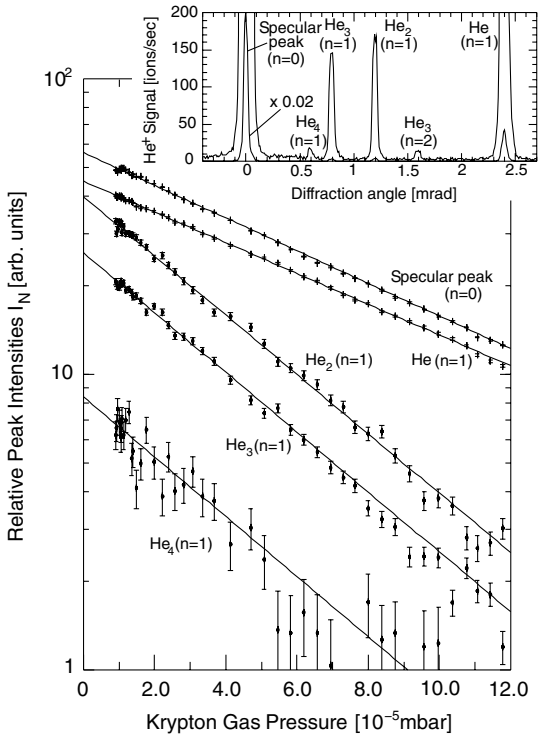

FIG. 2. Dependence of the specular and first order diffracted beam intensities (fitted areas under the peaks) on the Kr pressure in the scattering chamber measured for a cluster beam with a velocity of 415 m/s ($T_0 = 17$ K, $P_0 = 7$ bars). The inset shows the corresponding diffraction pattern.

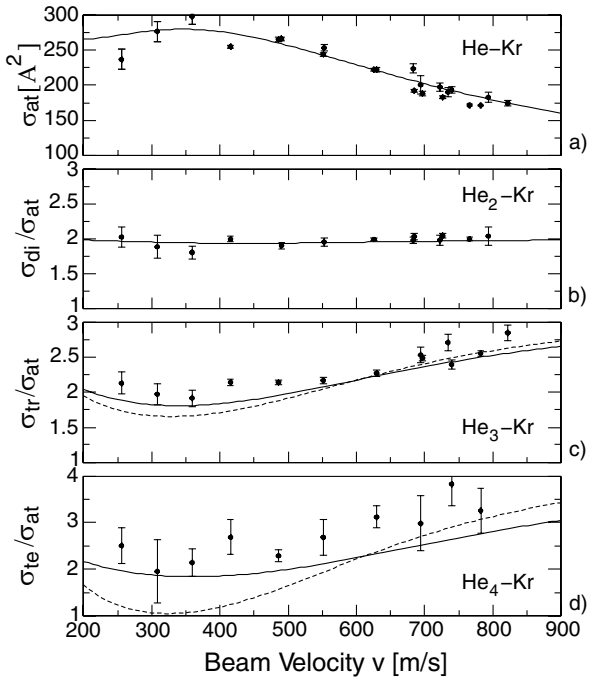

FIG. 3. (a) The measured total cross sections for scattering of a He atom from a Kr atom (experimental points) are adjusted to match calculations (solid line) for a Tang-Toennies potential model [19]. The measured ratios of He dimer, trimer and tetramer cross sections all with respect to the monomer cross section are shown in (b), (c), and (d), respectively. The solid line in (b) is calculated with a small ($\lesssim 5\%$) eclipse correction. The dashed lines in (c) and (d) include all double-impact eclipses, while the solid lines account in addition for all triple-impact eclipses.

center of mass frame should be smaller than the range of interaction of the projectile with each of the constituents, which in turn should be smaller than the average internuclear distance of the target constituents $\langle r_{ij}\rangle$. In our case this range is approximately given by $\rho = (\sigma_{at}/2\pi)^{1/2}$ and lies between 4.9 and 6.7 Å. In addition the velocity of the relative motion of the target constituents should be much smaller than the impact velocity. The former can be estimated from the average kinetic energies per atom listed in Table I to be between 14 and 61 m/s. These conditions are fulfilled for all three clusters.

Following Glauber, the elastic forward scattering amplitude for a Kr-He_2 collision with an incident wave vector k can be written in semiclassical approximation assuming straight line trajectories [14] as

$$F_{di}(0) = \frac{ik}{2\pi}\int d^{(3)}\vec{r}_{12}|\Psi_{di}(\vec{r}_{12})|^2\int d^{(2)}\vec{b}(1 - e^{i(\chi_1+\chi_2)}), \tag{2}$$

where the subscript "di" denotes quantities related to the dimer and the indices one and two denote the dimer atoms, the χ_1 and χ_2 are phase shifts due to the interactions with the separate particles one and two and depend on the impact parameter $\vec{b}$ and the internuclear distance $\vec{r}_{12}$, $\Psi_{di}(\vec{r}_{12})$ is the normalized wave function of the dimer ($\int d^{(3)}\vec{r}_{12}|\Psi_{di}(\vec{r}_{12})|^2 = 1$). The integration is carried out over all positions of the dimer atoms and over the two-dimensional impact parameter $\vec{b}$.

Since the overlap of the interaction regions of particles one and two can be neglected, the optical theorem after a change of variables of integration predicts for the dimer total scattering cross section [14]:

$$\sigma_{di} = \frac{4\pi}{k}\mathrm{Im}F_{di}(0) = 2\sigma_{at} + \frac{4\pi}{k^2}\mathrm{Re}\{f_{at}^2(0)\}\langle r_{12}^{-2}\rangle_{di}, \tag{3}$$

where σ_{at} is the He-Kr total scattering cross section, $f_{at}(0)$ is the complex elastic forward scattering amplitude and $\langle r_{12}^{-2}\rangle_{di}$ is the mean value of the inverse square of the distance between the atoms in the dimer.

The same procedure results in the following expressions for the total scattering cross sections of the more compact (Table I) trimer (index "tr") and tetramer (index "te"):

$$\sigma_{tr} = 3\sigma_{at} + 3\frac{4\pi}{k^2}\mathrm{Re}\{f_{at}^2(0)\}\langle r_{ij}^{-2}\rangle_{tr} + \Delta\sigma_{tr}, \tag{4}$$

$$\sigma_{te} = 4\sigma_{at} + 6\frac{4\pi}{k^2}\mathrm{Re}\{f_{at}^2(0)\}\langle r_{ij}^{-2}\rangle_{te} + \Delta\sigma_{te}. \tag{5}$$

The second terms on the right hand sides of Eqs. (4) and (5) account for all the possible *pairwise* eclipses within the complexes. Since Glauber judges that the approximations leading to Eq. (3) should be "roughly correct for internuclear distances down to the radii of the interaction regions themselves" they should also be valid for the trimer and tetramer [21]. The forward scattering amplitude $f_{at}(0)$ was calculated using a standard partial wave expansion for the same Tang-Toennies potential used to calculate the He-Kr cross section [19]. The $\langle r_{ij}^{-2}\rangle$ for the dimer, trimer, and tetramer were calculated using variational wave functions [9] and independently by Blume [22] and are reported in Table I. The final cross sections, averaged over the distribution of relative velocities assuming a Maxwellian distribution in the scattering cell, are shown in Fig. 3(b) as a solid line and in Fig. 3(c) and 3(d) as dashed line curves.

In the case of the dimer the average experimental ratio $\sigma_{di}/\sigma_{at} = 1.97 \pm 0.07$ is in excellent agreement with the theoretical value of 1.96 [Fig. 3(b)]. This implies that the Kr atoms are scattered from one or the other of the two He atoms and that the Kr atoms can even pass between the two He atoms without affecting the dimer bond despite its extreme weakness. The maximum experimental deviation of 3% from the ideal value of 2 places a lower limit on the mean internuclear distance: $\langle r_{ij}\rangle \geq 33$ Å, consistent with our earlier determination of 52 ± 4 Å [4].

In the case of the trimer the *pairwise* eclipse theory predicts a cross section which lies significantly below the experiments for $v \leq 650$ m/s. Thus the third term in

Eq. (4), which is proportional to the probability for all three particles of the trimer to be on a straight line (three atom eclipse), was also calculated following the original procedure of Glauber within the same set of approximations:

$$\Delta\sigma_{\rm tr} = -\frac{32\pi^3}{k^3}\,{\rm Im}\{f_{\rm at}^3(0)\}\int_0^\infty dz_1\int_0^\infty dz_2 \times[|\Psi_{\rm tr}(z_1, z_2, 1)|^2 + |\Psi_{\rm tr}(z_1, z_2, -1)|^2], \quad (6)$$

where $\Psi_{\rm tr}(r_1, r_2, \cos\theta_{12})$ is the wave function of the helium trimer [9], normalized in the same way as $\Psi_{\rm di}$, $\vec{r}_1$, and $\vec{r}_2$ are vectors, connecting two particles of the trimer with the third one, $\cos\theta_{12} = (\vec{r}_1 \cdot \vec{r}_2/r_1 r_2)$ is the angle between these two vectors, and z_1 and z_2 are projections of $\vec{r}_1$ and $\vec{r}_2$ on the direction of motion of the Kr atom.

The improved agreement [solid line in Fig. 3(c)] confirms the lineup probability as well as the extended Glauber eclipse theory and thus it can potentially shed light on the extensively discussed trimer geometry [11]. For the tetramer the triple-impact term makes a larger contribution and also improves the agreement [Fig. 3(d)]. The quadruple-impact correction was calculated to be less than 1%.

The good agreement with these ground state based calculations rules out significant concentrations of excited clusters which are expected to have considerably larger bond distances (Table I). Certainly excited trimers and tetramers are present in the early stages of the expansion, but downstream they probably break up or relax to the ground state. The small upward shift of the experimental with respect to the theoretical cross sections [Fig. 3(c)] might be due to a small ($\leq$15%) remaining concentration of Efimov trimers with cross sections $\sigma_{\rm tr}^* = 3\sigma_{\rm at}$.

In summary, these experiments demonstrate the transferability of nuclear physics scattering approximations to a many-body molecular scattering process, even though the trimer and tetramer have no simple analogs in nuclear physics [23]. The application of a multiple scattering theory with corrections only for shadowing due to eclipses avoids the many partial waves and convergence problems of the customary close-coupling approach [24]. With further improvements in the resolution and sensitivity it should be possible to extend these experiments to larger pure clusters and to small ^{4}He/^{3}He mixed clusters, which also have very weak binding energies.

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