

Atom Diffraction Reveals the Impact of Atomic Core Electrons on Atom-Surface Potentials

Vincent P. A. Lonij, Catherine E. Klauss, William F. Holmgren, and Alexander D. Cronin*

Department of Physics, University of Arizona, Tucson, Arizona 85721, USA

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We measured ratios of van der Waals potential coefficients (C_3) for different atoms (Li, Na, K, and Rb) interacting with the same surface by studying atom diffraction from a nanograting. These measurements are a sensitive test of atomic structure calculations because C_3 ratios are strongly influenced by core electrons and only weakly influenced by the permittivity and geometry of the surface. Our measurement uncertainty of 2% in the ratio C_3^K/C_3^{Na} is close to the uncertainty of the best theoretical predictions, and some of these predictions are inconsistent with our measurement.

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Calculations of atomic polarizability (α) and van der Waals (vdW) potential coefficients (C_6 and C_3) are in demand for predicting pressure-induced and black-body shifts for atomic clocks, scattering lengths in Bose-Einstein condensates, and binding energies for molecules [1–4]. Related calculations are also needed to interpret atomic parity violation as a test of the standard model [5,6]. However, calculating these quantities is challenging because including core electrons, as opposed to considering only the valence electrons, requires modeling many-body interactions in a quantum system with relativistic corrections. Fortunately, these quantities (α , C_3 , and C_6) are interrelated and can each be expressed in terms of dipole matrix elements. Therefore, measurements of any one of these quantities, even for a few atomic species, can help test the calculation methods that are used to predict all of these quantities for several different species.

Both dc polarizability (α_0) and van der Waals atom-atom potential coefficients (C_6) have been used previously as benchmarks for atomic theory calculations [6,7]. Until now, however, it has been difficult to use vdW atom-surface potential coefficients (C_3) as a benchmark because of shifts and uncertainties in C_3 due to unknown properties of the surface [8]. We have overcome this problem by studying ratios of C_3 for different atoms.

In this Letter, we show that ratios of interaction strengths for Li, Na, K, and Rb atoms interacting with a surface depend very weakly on the permittivity and geometry of the surface, provided that the atoms interact with the *same* surface. This allows us, for the first time, to use measurements of atom-surface interactions to distinguish between atomic structure models. The ratios of C_3 reported here constitute the first experimental detection of the contribution of core electrons to C_3 .

Indeed, measurements of C_3 can serve as an excellent benchmark for atomic structure calculations because core electrons contribute more to C_3 coefficients than to C_6 or α_0 [9]. In Rb, for example, 3% of α_0 is due to core electrons and calculations of α_0 have an uncertainty of 0.1%. By comparison, in vdW interactions between Rb and

an ideal surface, 35% of C_3 is due to core electrons and calculations of C_3 have an uncertainty of 1%–2% [7,10].

We will first briefly describe our experiment and explain how ratios of C_3 are measured. Next we will explain why surface composition has a very small effect on C_3 ratios. Finally we compare calculations from several different atomic structure models to our measurements.

Our experimental setup is described in detail elsewhere [11,12]. In brief, we studied diffraction of supersonic beams of Li, Na, K, or Rb atoms incident on a 100-nm period silicon nitride (SiN_x) nanograting. vdW interactions between the atoms and the grating bars affect the relative intensities of the far-field diffraction orders. We adjust the velocity of the atom beam by changing between carrier gas mixtures in order to study the intensities of far-field diffraction orders as a function of velocity (see Fig. 1).

Earlier experiments using nanogratings reported absolute measurements of C_3 [11–14]. However, because

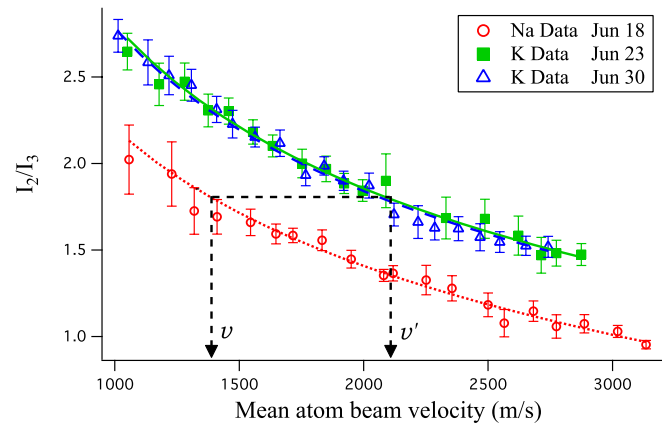


FIG. 1 (color online). Measurements of the relative diffraction intensity of the 2nd and 3rd diffraction orders (I_2/I_3) for Na and K. Ratios of the potential strengths can be obtained from these data by finding two velocities v and v' such that $(I_2/I_3)^{Na} = (I_2/I_3)^K$. The arrows indicate two such velocities $v = 1390$ m/s and $v' = 2100$ m/s. We find $C_3^K/C_3^{Na} = v'/v = 1.51$. We obtained a more precise ratio by fitting the data [19].

different experiments used different samples, ratios of these previous experiments do not provide the same precision as the directly measured ratios presented here. For high precision ratio measurements it is essential to study the exact same surface sample since both geometry and composition may vary from sample to sample. To achieve this, we take care to illuminate the same 100 grating bars with each of our different 10- μm wide atomic beams.

We first show how the ratios of C_3 can be obtained from our experimental data without needing to know the geometry of the grating (period, open fraction, and bar shape) or the shape of the potential [15]. For a real surface that has significant roughness or a layer of contamination, the van der Waals potential may differ from the ideal form $V = -C_3 r^{-3}$, where r is the distance to the surface [16]. Furthermore, for a surface of finite extent, such as our nanogratings, the potential near the edges of the grating bars is a function of multiple spatial coordinates. We therefore consider a more general form for the potential,

$$V_{\text{vdW}} = -C_3 f(x, z), \quad (1)$$

where x is parallel to the grating k vector and z is the direction of atom propagation. Since the grating bars are relatively uniform in the y direction, we assume that V is independent of y . Although we still assume that the potential is proportional to C_3 , the only restriction we put on $f(x, z)$ is that it be the same for all atoms. This is true by construction in the pairwise interaction (PWI) approximation [8,17], so we only require that deviations from the PWI approximation are proportional to C_3 and the same for all atoms. For the simple geometry of our gratings, this is a reasonable approximation [12].

As in previous work, we model the grating as a thin phase and amplitude mask [11–13]. The incident atom beam is approximately a plane wave, so the wave function just beyond the grating is given by $\psi(x, z) = a(x) \times \exp[ik_z z + i\phi_{\text{vdW}}(x)]$, where $a(x)$ accounts for absorption by the nanostructure and ϕ_{vdW} is a phase induced by the atom-surface potential. Propagation in the free space beyond the grating results in a set of equally spaced diffraction orders in the far field. If both $a(x)$ and $\phi_{\text{vdW}}(x)$ are periodic with period d , then the intensity of the n th order (relative to the incident intensity) is given by

$$I_n = \left| \frac{1}{d} \int_{-d/2}^{d/2} a(x) \exp[i\phi_{\text{vdW}}(x) + i2\pi n x/d] dx \right|^2. \quad (2)$$

Note that the only atom-specific quantities are contained in ϕ_{vdW} . In the Raman-Nath approximation ϕ_{vdW} is given by

$$\phi_{\text{vdW}}(x) = \frac{C_3}{\hbar v} \int_{z_0}^{z_f} f(x, z) dz, \quad (3)$$

where v is the velocity of the atoms and z_0 and z_f are positions before and after the grating, respectively.

Since the only quantity that changes between different experiments on the same grating is C_3/v , any experiment

using the same grating and the same C_3/v will produce the same diffraction intensities. For two species with C_3 and C'_3 , respectively, this implies

$$I_n(v) = I'_n(v') \quad \text{with} \quad v' = v C'_3 / C_3. \quad (4)$$

We can therefore determine the ratio of potential strengths directly by finding two velocities v and v' that yield the same diffraction intensities for two different atomic species (as indicated in Fig. 1).

Rather than studying simply the diffraction intensities I_n , we focus on the relative intensity I_2/I_3 . Studying relative intensities reduces systematic errors associated with detector nonlinearity, the beam profile used to fit the diffraction data, and fluctuations in the incident beam intensity. We choose the 2nd and 3rd orders because they are more sensitive to C_3 than the 0th and 1st orders and more easily detectable than higher orders. Figure 1 shows I_2/I_3 as a function of velocity for K and Na. The measured ratios for Li, Na, K, and Rb are given in Table I.

The assumptions of Eq. (1) are considerably more general than in previous work with nanogratings. It is therefore worthwhile to verify experimentally that our measurements are independent of geometry. We repeated our measurements using gratings with different grating bar widths as well as gratings that were rotated by several degrees. This yielded different diffraction intensities, but the reported ratios of C_3 remained unchanged. The reproducibility of our experiment is consistent with the uncertainties obtained from fitting the data in Fig. 1. For more details regarding the uncertainties reported in Table I, see [19].

We now show why the surface composition only has a small effect on the ratios of C_3 . The vdW coefficient is given in the nonretarded regime by

$$C_3 = \frac{\hbar}{4\pi} \int_0^\infty \alpha(i\omega) g(i\omega) d\omega, \quad (5)$$

where $\alpha(i\omega)$ is the atomic polarizability. The function $g(i\omega)$ describes the surface response and is given by $g(i\omega) = [\epsilon(i\omega) - 1]/[\epsilon(i\omega) + 1]$, where $\epsilon(i\omega)$ is the electric permittivity of the surface.

In order to explore the effect of the surface, it is instructive to consider the simplified model proposed by Vidali and Cole that uses single-oscillator expressions for both the atom and the surface [20]. The integral in Eq. (5) can then be solved exactly:

TABLE I. Measured ratios of C_3 compared to theory. The theoretical values are obtained using many-body calculations for $\alpha(i\omega)$ and a Tauc-Lorentz model for a SiN_x surface [16,18].

| Ratio | Theoretical prediction | This measurement |
|-----------------------------------|------------------------|-------------------|
| $C_3^{\text{Li}}/C_3^{\text{Na}}$ | 0.896 | 0.89 ± 0.04 |
| $C_3^{\text{K}}/C_3^{\text{Na}}$ | 1.51 | 1.544 ± 0.025 |
| $C_3^{\text{Rb}}/C_3^{\text{K}}$ | 1.13 | 1.12 ± 0.04 |
| $C_3^{\text{Rb}}/C_3^{\text{Na}}$ | 1.69 | 1.72 ± 0.07 |

$$C_3 = \hbar\alpha_0 g_0 \frac{\omega_0 \omega_s}{8(\omega_0 + \omega_s)}, \quad (6)$$

where ω_s is the surface-plasmon frequency and ω_0 is the frequency of the Lorentz oscillator used to model the atom. For alkali atoms near a SiN_x surface, $\omega_0 \ll \omega_s$, and we may make the approximation

$$C_3 \approx \hbar\alpha_0 g_0 \omega_0 / 8. \quad (7)$$

In the case of a perfect conductor ($\omega_s \rightarrow \infty$), Eq. (7) becomes exact.

For a material with finite conductivity, the first-order correction to Eq. (7) is of order ω_0/ω_s . The corresponding correction to the ratio C_3/C_3^i for two atoms with ω_0 and ω_0^i is of order δ/ω_s , where $\delta = \omega_0 - \omega_0^i$. For Na and K in our experiments, $\hbar\delta \approx 0.3$ eV and for a SiN_x surface $\hbar\omega_s \approx 13$ eV, so the effect of the surface on the ratio C_3^K/C_3^{Na} should be less than 2%. We verify this below with more realistic descriptions of $g(i\omega)$ and $\alpha(i\omega)$.

Because of Eq. (7), it is enlightening to plot the relative potential strengths C_3^i/C_3^{Na} versus the quantity $(\alpha_0\omega_0)^i/(\alpha_0\omega_0)^{\text{Na}}$, with $i \in \{\text{Li, K, Rb}\}$ (see Fig. 2). We plot the ratios relative to Na because our atom beam works best with Na, which thus gives the most accurate reference. It is evident from Fig. 2 that Eq. (7), i.e., the case of a single-oscillator atom near a perfectly conducting surface, is not an adequate description of the current experiment. Instead, our measurements are consistent with a model that includes atomic core electrons.

To emphasize the utility of ratio measurements we investigate five different models for the surface and two different models for the atom. We considered the Tauc-Lorentz model [21] with three different parametrizations to describe a SiN_x surface [18,22,23]. For comparison, we also considered a Drude model for a gold surface as well as a perfect conductor. For the atom we compare two different

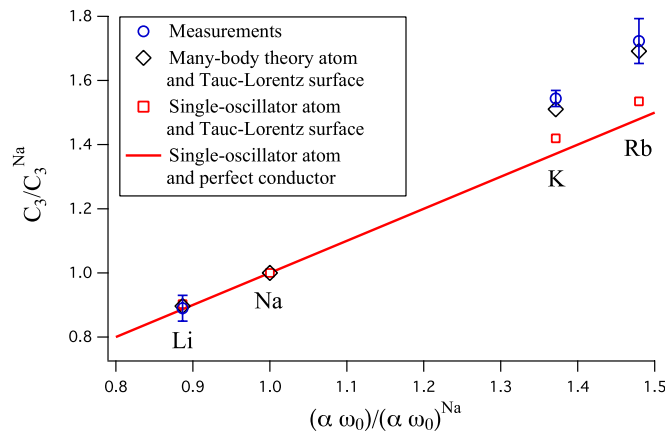


FIG. 2 (color online). Experimentally determined ratios of potential strength relative to Na (C_3/C_3^{Na}). The solid line with slope of 1 and intercept of 0 is the prediction for a single-oscillator atom near a perfect conductor [Eq. (7)]. The figure also shows results from a many-body calculation for the atom [16] and Tauc-Lorentz model for the surface [18].

models: a single-oscillator model and the model provided by Derevianko *et al.* that includes core electrons [7,16]. We list the results in Table II.

The range in C_3 due to different models of SiN_x illustrates the problems we have overcome by studying ratios. Including core electrons in the description of the atom increases the predictions for C_3^{Na} by about 6% and for C_3^{K} by 12%. Since different models for the SiN_x surface cause shifts of about 6% for both atoms, it has been hard to use direct measurements of C_3 for one atomic species to distinguish between different models for the atom.

The main point of this Letter is that the ratio $C_3^{\text{K}}/C_3^{\text{Na}}$ varies by only 1% between the different SiN_x models while the different atomic models still yield shifts of 6%. This means we have found a remarkable situation in which ratios are not only easier to measure, but are more useful to study because predictions of ratios are relatively insensitive to the type of surface used.

Theoretical predictions of C_3 in the literature are typically given for the case of an atom interacting with a perfect conductor. Table II shows that, although our ratios do not vary much between the different realistic surface models, a theory that includes core electrons and assumes an ideal surface still overestimates the ratio $C_3^{\text{K}}/C_3^{\text{Na}}$ for a real surface by about 2%. This is because heavier atoms have additional core electron excitations at higher frequencies. Note that this correction to the ratio is 50 times smaller than the corresponding correction for absolute measurements.

Table III shows a summary of recent theoretical predictions of the ratio $C_3^{\text{K}}/C_3^{\text{Na}}$ found in the literature; all these theories assume an ideal surface. Therefore, we expect the predictions in Table III need to be decreased by about 2% before we can compare them to our experiment that used a real surface.

After this adjustment, our measurement $C_3^{\text{K}}/C_3^{\text{Na}} = 1.544 \pm 0.025$ is inconsistent with the effective core

TABLE II. Theoretical predictions of C_3 for Na and K in eV \AA^3 and their ratios resulting from different models for the surface and the atoms.

| Surface model | Atom model | C_3^{Na} | C_3^{K} | $C_3^{\text{K}}/C_3^{\text{Na}}$ |
|---------------------|-------------------|-------------------|------------------|----------------------------------|
| SiN_x [22] | Single-oscillator | 3.34 | 4.70 | 1.407 |
| SiN_x [18] | Single-oscillator | 3.17 | 4.50 | 1.420 ^a |
| SiN_x [23] | Single-oscillator | 3.31 | 4.67 | 1.409 |
| Gold [24] | Single-oscillator | 4.76 | 6.92 | 1.455 |
| Perfect conductor | Single-oscillator | 6.25 | 8.61 | 1.375 ^a |
| SiN_x [22] | Many-body [16] | 3.48 | 5.27 | 1.514 |
| SiN_x [18] | Many-body [16] | 3.28 | 4.95 | 1.510 ^a |
| SiN_x [23] | Many-body [16] | 3.44 | 5.20 | 1.512 |
| Gold [24] | Many-body [16] | 4.84 | 7.31 | 1.510 |
| Perfect conductor | Many-body [16] | 7.54 | 11.6 | 1.548 |

^aThese values are also shown in Fig. 2.

TABLE III. Summary of theoretical predictions of the ratio C_3^K/C_3^{Na} found in the literature, assuming a perfectly conducting surface. To compare these values to our measurement, $C_3^K/C_3^{\text{Na}} = 1.544 \pm 0.025$ for a real surface, the theoretical values must be reduced by about 2%. MBPT stands for many-body perturbation theory and SD refers to the single-double method.

| Method | Reference | C_3^K/C_3^{Na} |
|-------------------------------------|---------------|-------------------------|
| Effective core potential | [25] | 1.37 |
| Third-order MBPT | [26] | 1.50 |
| All-order many-body (SD) | [26] | 1.52 |
| Direct integration of α (SD) | [7] Method II | 1.53 |
| Direct integration of α | [7] Method I | 1.55 |
| Integration of tabulated α | [16] | 1.55 |
| Semiempirical | [27] | 1.56 |

potential model of Ref. [25] and third-order many-body perturbation theory [26]. Our experiment is in best agreement with values based on the direct integration of $\alpha(i\omega)$ in Refs. [7,16] and the semiempirical approach in Ref. [27].

In summary, by measuring diffraction intensities of a supersonic atom beam from a material transmission grating we were able to make precision measurements of ratios of C_3 for Li, Na, K, and Rb interacting with the same surface. We showed that these ratios are insensitive to the material composition of the grating. Since the ratios of C_3 no longer depend on the specific nature of some exotic surface such as SiN_x , this measurement is suitable as a benchmark for atomic physics calculations. We report the ratio C_3^K/C_3^{Na} with 2% precision, which is sufficient to distinguish between some theoretical predictions.

It is possible to extend our method to a range of atomic and molecular species because our method does not rely on species-specific equipment such as resonant lasers [14]. There are several systems for which our method can provide a benchmark that would advance the current state of the art. The ratio $C_3^{\text{Sr}}/C_3^{\text{Na}}$, for example, varies by 4% between different theoretical predictions [16,27]. Uncertainties in C_3 for Yb and metastable Sr are estimated to be significantly larger [1,28,29]. vdW potentials are also a significant source of uncertainty in computing binding energies of molecules to surfaces [30]. All these systems are therefore attractive candidates for future ratio measurements.

*cronin@physics.arizona.edu

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