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Spectroscopic detection of atom-surface interactions in an atomic-vapor layer with nanoscale thickness

K. A. Whittaker,1 J. Keaveney,1 I. G. Hughes,1 A. Sargsyan,2 D. Sarkisyan,2 and C. S. Adams1
1Joint Quantum Centre (JQC) Durham-Newcastle, Department of Physics, Durham University, South Road, Durham, DH1 3LE, United Kingdom
2Institute for Physical Research, National Academy of Sciences, Ashtarak 2, 0203, Armenia

We measure the resonance line shape of atomic-vapor layers with nanoscale thickness confined between two sapphire windows. The measurement is performed by scanning a probe laser through resonance and collecting the scattered light. The line shape is dominated by the effects of Dicke narrowing, self-broadening, and atom-surface interactions. By fitting the measured line shape to a simple model we discuss the possibility to extract information about the atom-surface interaction.

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I. INTRODUCTION

Atomic alkali-metal vapor cells are widely used in applications ranging from magnetometry [1], sources of quantum light [2], electric-field imaging [3], atomic clocks [4], nanophotonics [5], optical isolators [6], and quantum memory [7]. Modern vapor cell technology has been trending towards integrating miniaturized cells into the aforementioned applications, with millimeter [8–11], micron [12], and even nanometer scale cells [13] popular areas of investigation. An accurate method of analyzing spectra from miniature cells is vital to aid the development of such technology.

If the vapor is confined spatially with a dimension less than the transition wavelength fascinating physical effects become accessible such as the narrowing of spectral lines [14], extreme dispersion resulting in large negative group indices and superluminal propagation [15,16], repulsive van der Waals interactions [17], the cooperative Lamb shift [18], and perhaps a medium where the Kramers-Kronig relations are violated [19].

The tight confinement of the atoms inside nanocells opens up opportunities to study the interaction of atoms with a nearby surface, explored using spectroscopy on both low-lying [20] and higher-lying excited states [21] or EIT spectroscopy of highly excited Rydberg states [22]. This can be expanded to investigate the temperature dependence of the coefficients describing the strength of the atom-surface (AS) interaction [23] and cases where the usually attractive AS interaction becomes repulsive due to surface resonances [17]. Alternative methods to spectroscopy for probing the AS interaction have also been used, such as scattering or deflection of a beam close to a surface [24–29], atomic beam diffraction [30,31], and reflection of an ultracold atom cloud from an atomic mirror [32,33].

In this paper we employ spectroscopic measurements that allow us to infer the effects of the AS interaction at the time of absorption. Note that in this case, both ground and excited states contribute to the measurement of the AS interaction. In what follows we present detailed spectra for a range of cell lengths and temperatures, expanding upon a previous publication [20], and inspired by discussion points raised in [34], giving further detail into the error analysis and fitting procedures, present a simulation justifying the model used to describe velocity selective effects used, and offer further analysis on the results found. We describe an experiment that takes many absorption spectra over a range of temperatures and cell lengths, and uses fitting and error analysis to precisely measure the general form of the AS interaction within the near field. We first detail the methods of data acquisition for absorption spectra, where we utilize single-photon counting modules (SPCMs) to acquire absorption spectra over long integration times. The ease of acquisition allows us to take many spectra for a range of cell lengths and temperatures.

The experiment section details the form of the AS interaction in the near field (van der Waals) regime [35], discussing possible effects that may alter the final form, such as a transition between the near field and retarded (Casimir-Polder) [36] regimes; the effect of multiple reflections, and the effect of temperature on the interaction. We then give an overview of the fitting procedure performed on the spectra taken. The model we have developed accounts for self-broadening [37], Dicke narrowing effects [14], and the AS interaction [35]. The Results section presents fitting results for spectra taken on the Rb $D_2$ line and the Cs $D_1$ line, where we find that to describe spectra in the length range investigated herein, the van der Waals description of the AS interaction is optimal. We finally discuss the implication and accuracy of our results including a discussion of the limitations of the technique and perspectives for further work.

II. EXPERIMENT

A. Data acquisition

To probe the atom-surface (AS) interaction we use nanocells (NCs), produced at the National Academy of Science in Armenia [13]. The cells are made from $c$-axis
aligned sapphire with an interior surface roughness of 3 nm and are described in more detail in previous publications [15,18,38,39]. Each cell has a wedged profile, with a thickness range of 2 μm to 30 nm. In order to exploit variable vapor column thickness in the range of 30–2000 nm, the cell is vertically wedged by placing a 2-μm-thick platinum spacer strip between the windows at the bottom side prior to gluing.

The NC thickness $L$ is measured using back reflections from the surfaces inside the cell. Two back reflections $R_1$, from the front surface of the cell, and $R_2$, a combination of reflections from both interior surfaces, are measured. Etalon effects inside the cell mean the two beams that compose $R_2$ interfere constructively or destructively depending on the cell length, resulting in a varying intensity of $R_2$. The thickness is calculated by taking the ratio of intensities $R_1$ and $R_2$ and applying a standard Fabry-Perot treatment [40].

Our method measures absorption or more precisely extinction in the forward scattering direction by detecting the off-axis scattered light resulting in absorption spectra that we can fit to measure the AS interaction. We use this method because a measurable transmission profile for extremely short cell lengths can only be obtained by heating to high temperatures (exceeding 300 °C), where collisional broadening smears out potential atom-surface measurements [37]. For shorter cell lengths ($L < 100$ nm) and lower temperatures ($T < 200$ °C), absorption is less than 0.5% of the incident light, making the measurement of transmission impractical. Using off-axis detection of scattered light with single-photon counters, extremely high sensitivity spectra can be taken from shorter cell lengths at lower temperatures. This increases our experimental resolution as spectra with all hyperfine states resolved can be taken using single-beam spectroscopy. The narrowing of the lines is caused by Dicke narrowing [14] effects inside the cell—a motional effect that will be outlined in Sec. III. Absorption spectra were taken on the Rb $D_2$ line, used for its large AS interaction on the ground-state transition, and the Cs $D_1$ line, used for its large 9-GHz ground-state splitting and 1.2-GHz excited-state splitting, much larger than the Doppler width. All spectra were taken within the weak-probe limit [41].

The experimental layout is shown in Fig. 1. Some of the light is sent through reference optics—a 7.5 cm reference vapour cell and a Fabry-Perot etalon, which are collected concurrently with the scattered light spectra to calibrate the laser frequency. The light is then sent down an optical fiber to the NC section of the experiment, where lens L1 focuses the beam to a 1/e² radius of 20 μm inside the NC. The transmitted beam is recollimated by lens L2 and a transmission spectra is collected on photodiode PD. Off-axis scattered photons are collimated by lens L3, with ambient light filtered out by an infrared (IR) filter, and sent into a single-photon counting module (SPCM) via a fiber collimator FC1. The signal is processed by the oscilloscope to generate a histogram of the photon arrival times.

The laser scan time is 50 ms, and individual bins in the histogram are 5 μs long, corresponding to a bin width of 2 MHz. Hence the detection method is sensitive to the frequency at which a photon was absorbed, meaning AS shifts measured map directly onto a particular AS separation for that frequency. This renders our method insensitive to any transient effects such as motion between the time of absorption and fluorescence events or interruption of fluorescence decay by wall collisions [34]. Single scans return only a few photon counts, so long integration times (15 min to several h) are used to build up statistics of arrival times, allowing for sensitive detection of spectra.

Figures 2(a) and 2(b) show examples of raw spectra taken for $T = 125$ °C. The data are taken at two different cell lengths, 60 nm (red area) and 250 nm (blue area). The raw spectra have a very large background count, highlighted in grey. Signal-to-background ratio varies hugely between different cell lengths, only the atomic signal is highlighted (colored areas) in Figs. 2(a) and 2(b). The effect of these background counts on experimental errors will be discussed in the next subsection. Before analysis, the background signal is subtracted from the atomic signal. The resulting processed data are shown as black points in Figs. 2(c) and 2(d). We fit the spectra, using a procedure outlined in Sec. III. Examples of fit results are shown on Fig. 2(c) ($L = 60$ nm, red line) and 2(d) ($L = 250$ nm, blue line).

**B. Error analysis**

The errors in the atomic signal, $A(\omega)$, are calculated by taking the frequency-dependent raw spectrum $R(\omega)$ and subtracting the background count $B$,

$$A(\omega) = R(\omega) - B. \quad (1)$$

FIG. 1. (Color online) Experimental schematic used to measure the atomic line shape. The laser is scanned through resonance and we detect the scattered light. Part of the beam is split off by a half-wave plate ($\lambda/2$) and polarizing beam splitter cube (PBSC) to the reference optics for frequency calibration. The beam is then fibered to the nanocell (NC) section of the experiment, where lens L1 focuses the beam to a 1/e² radius of 20 μm inside the NC. The transmitted beam is recollimated by lens L2 and a transmission spectra is collected on photodiode PD. Off-axis scattered photons are collimated by lens L3, with ambient light filtered out by an infrared (IR) filter, and sent into a single-photon counting module (SPCM) via a fiber collimator FC1. The signal is processed by the oscilloscope to generate a histogram of the photon arrival times.
For the analysis performed on Rb spectra, we take an average of the fitted parameters weighted by the reduced $\chi^2$ squared of the fit. The reduced $\chi^2$ squared is a goodness of fit measurement, represented here with $\Upsilon$ to avoid confusion with the vapor susceptibility. $\Upsilon$ is calculated as

$$\Upsilon = \frac{1}{v} \sum_{\omega} \frac{(A(\omega) - T(\omega))^2}{\sigma^2_A}.$$  \hspace{1cm} (3)

where $A(\omega)$ is the observed frequency-dependent atomic signal, $T(\omega)$ is the theoretical signal, and $v$ is the degrees of freedom, calculated as $v = N_{\text{points}} - N_{\text{param}}$, where $N_{\text{points}}$ is the length of the data set and $N_{\text{param}}$ is the number of fitted parameters.

Values for $\Upsilon$ of our fitted spectra vary between 0.1 to over 1000. Generally, a $\Upsilon$ close to 1 indicates a good fit, and any value much lower than 1 indicates overestimated errors [42]. However, this is not the case in our experiment; the smaller values of $\Upsilon$ are caused by the huge background counts for shorter cell lengths, illustrated in Figs. 2(a) and 2(b). The small values of $\Upsilon$ can be accounted for by considering the large relative error margins that arise when the atomic signal is small resulting in a higher proportion of the fitted spectra within the error margins of the atomic signal. Consequently, the resulting $\Upsilon$ is much less than 1, but still a valid measure of goodness of fit.

### III. Theory and Fitting

#### A. Atom-surface interaction

The atom-surface (AS) interaction is the attraction between a dipole and its reflection in a surface. An induced dipole in the atomic medium induces a shift of charge in a nearby conducting or dielectric surface [35]. This charge redistribution results in a virtual dipole image [36], which has an attractive interaction with the original atomic dipole. This causes a redshift of the atomic transitions, generally described using $-C_\alpha/r^\alpha$, where $\alpha$ is an exponent that varies between 3 and 4, depending on the interaction regime.

The Casimir-Polder (CP) interaction describes this process at AS separations $r > \lambda/2\pi$, where $\lambda$ is the transition wavelength. The interaction between the real and image dipole is retarded by the transit time of photons [35], and the potential takes the form $U_{\text{CP}} = -C_4/r^4$, with $C_4$ as a coupling coefficient determining the strength of the interaction.

When the AS separation reaches the regime $r < \lambda/2\pi$, the induced shifts follow the van der Waals (vdW) description

$$U_{\text{vdW}} = -C_3/r^3,$$

where $C_3$ is the coupling coefficient of the van der Waals interaction. Figure 3(a) shows the induced red shift caused by $U_{\text{vdW}}$.

$C_3$ is dependent on the atomic polarizability [43], and hence varies depending on the electronic transition the shift is acting upon. When measuring the AS shift on an optical transition, the effective coupling coefficient is the difference between the ground and excited states. For this reason, we distinguish between coupling coefficients using a superscript denoting the transition, e.g., $C_3^{5S_{1/2}}$ for the $^{85}\text{Rb}$ $5S_{1/2}F_g = 2,3$ ground states and $C_3^{5S_{1/2}ightarrow 5P_{3/2}}$ for measurements taken on the $^{85}\text{Rb}$ $5S_{1/2}F_g = 2,3$ to $5P_{3/2}F_e = 1,2,3,4$ transition.
The smooth transition between the vdW (near field) and CP regime [44] has been the subject of many studies [36,43,45], with estimates for the onset of the transition ranging from lengths of $\lambda/2\pi$ [43] to 0.03$\lambda$ [46]. To identify the length regime our work covers, we inspect the full form of the AS interaction including both CP and vdW forms [43]:

$$U_{AS} = -\frac{\hbar^2}{2M} \left[ \frac{r^3}{\beta_3} + \frac{r^4}{\beta_4} \right]^{-1},$$

where $M$ is the atomic mass and $\beta_3, \beta_4$ are length parameters related to the strength of the vdW/CP potential and are taken from [43]. Values taken are for ground state Rb ($5S_{1/2}$), unlike the transitions we investigate experimentally, which probe the difference in interaction coefficients between the ground ($5S_{1/2}$) and excited ($5P_{3/2}$) states. Calculation of $\beta_3, \beta_4$ for the excited-state transitions are beyond the scope of this study, and we use the information from Fig. 3(b) as an indicator for which interaction regime we expect our spectra to lie in. We expect that the ground-state case is a worst case scenario as we are further into the C$_3$ region for the excited state as the transition wavelengths to nearby states are longer. Figure 3(b) shows the resulting potential for the ground state (purple line). The length scale $\tilde{r}$ is scaled in units of $\lambda/2\pi$. $U_{vdW}$ is normalized such that $U_{vdW} = 1$ at $\tilde{r} = 1$. Both the CP and vdW interactions are plotted for comparison (blue dot-dashed and red dotted lines respectively). The length range that most of our data are produced for is shown as a gray area on the plot. In Fig. 3(c) we plot the length dependence of the exponent $\alpha$ of the AS interaction. Figures 3(b) and 3(c) demonstrate that our experiment is sensitive to the shorter range van der Waals interaction regime. The average exponent in the length range $L = 10$–40 nm is $\alpha = 3.16$.

The impact of the AS interaction on the final resonance line shape is usually an overall redshift of the line shape, accompanied by a long asymmetric red tail due to atoms at different positions inside the cell experiencing a different shift. However, if surface polaron resonances coincide with the atomic resonance, the AS interaction becomes repulsive, instead causing a blueshift of the atomic resonance [17].

The values of $C_3$ measured in this experiment are for the Rb $5S_{1/2} \rightarrow 5P_{3/2}$ transition. The $C_3$ coefficient for the transition when the atoms are interacting with a perfectly conducting surface is $C_3^{5S_{1/2}\rightarrow 5P_{3/2}} = 4.1 \pm 0.2$ kHz $\mu$m$^3$ [47], calculated using the methods outlined in [48]. When the surface is not a perfect conductor, $C_3$ is multiplied by a reflection coefficient $R$ [49]. Sapphire has no significant variation in the frequency-dependent permittivity $\epsilon(\omega)$ in the relevant frequency range, and hence we use a value of $\epsilon_{sapph}(\omega) = 3.24$ for the Cs $D_1$ and Rb $D_2$ line, hence the reflection coefficient can be expressed as $R = [\epsilon_{sapph}(\omega) - 1]/[\epsilon_{sapph}(\omega) + 1]$. This results in a scaling factor of 0.53 for values of $C_3^{5S_{1/2}\rightarrow 5P_{3/2}}$ measured in this experiment.

The coupling coefficient $C_3$ also varies with temperature [23,44]. However at short ranges the thermal dependence of $C_3$ is dominated by surface excitations [23]. This is not the case for the transitions investigated herein, as they do not concur with the frequencies of any surface plasmon excitations of sapphire [49]. There is still some temperature variation of the $C_3$ coefficient; this is on the order of 1% over the temperature ranges investigated herein and is hence negligible in the scope of this experiment [47].

The AS interaction is also affected by multiple reflections in the surface, where the induced dipole interacts with reflections at integer multiples of the AS separation $r$. The effect of such reflections are shown in the inset to Fig. 3(a). The potential from a single reflection (blue line) differs only slightly from the effect of two (purple dotted line), three (red dashed line), and four (green dot-dashed line) reflections. These differences
are on the order of a few hundred kHz, smaller than detectable in the experiment.

**B. Line shapes for absorption spectra in nanometric cells**

We analyze the raw data using a model developed to describe the susceptibility of an alkali-metal vapor. The fitting function calculates the detuning-dependent susceptibility $\chi(\Delta)$ of the vapor, then converts it to an absorption spectrum, using a process similar to that outlined in [50]. The elements included in the model are outlined in Fig. 4. Each step is illustrated with an example line shape with the most relevant equation displayed beneath it. For comparison, the state of the line shape after (before) each step is shown in red (gray).

The first step is calculating an initial spectrum containing the natural linewidth $\Gamma_0$ for each hyperfine transition, shown in Fig. 4(a). Each transition is an independent two-level system. We then sum over all transitions. The single two-level susceptibility is given by [51]

$$\chi(\Delta) = \frac{iK}{\Gamma_0/2 - i\Delta}.$$  

where $\Delta$ is the detuning and $K$ is a proportionality constant that includes the dipole matrix element and transition strengths. Atomic data including the natural linewidth, dipole matrix element, transition strengths, and level splittings are taken from [37]. The density is calculated from the measured temperature using the proportionality constant, using values from [37]. The density is determined by the gas pressure formulas in [50]. We assume we are within the collision regime where the binary approximation is valid. This is accounted for in the model by including it in the calculation of the susceptibility for single transitions, replacing $\Gamma_0$ in Eq. (5) with $\Gamma_{tot}$, where $\Gamma_{tot} = \Gamma_0 + \Gamma_{col}$. The line shape is then summed over all transitions to generate a spectrum describing the natural line shape broadened by interatomic collisions.

Next, we account for velocity-dependent effects, illustrated in Fig. 4(c). In longer cells, the unrestricted motion of atoms in all directions leads to a Doppler broadening of the spectral lines. However, the tight confinement of the NC restricts the motion of atoms in the propagation direction, altering velocity-dependent shifts seen in the spectra. Atoms with a low velocity vector in the direction of laser beam propagation have a longer interaction time and therefore dominate the signal.

The velocity selected line shape can be understood by exploring the effect of the cell geometry on the atom-light interaction, illustrated schematically in Fig. 5(a). The NC is much shorter than the mean free path of the atoms, hence atoms traveling perpendicular to the windows with a high velocity in the direction of beam propagation $v_z$ collide with the opposite wall frequently, suppressing their contribution to the signal [52]. Atoms traveling at a small angle $\theta$ to the wall with a low $v_z$ have a much longer interaction time, and a much smaller Doppler shift. These “slow” atoms undergo more absorption relative to the “fast” atoms, resulting in enhanced sub-Doppler features on top of a small Doppler-broadened background in NC spectra.

Figure 4(b) shows the effects of collisional broadening, a density-dependent broadening caused by interatomic collisions. When an atom in the excited state undergoes a collision with another atom, there is a probability of the excited atom returning to the ground state. This results in a reduction of the lifetime leading to a homogeneous broadening of the spectral lines that is linearly dependent on density $N$ [51]. We model the collisional broadening $\Gamma_{col}$ as $\Gamma_{col} = \beta N$, where $\beta$ is a proportionality constant, using values from [37]. The density is calculated from the measured temperature using the vapor pressure formulas in [50]. We assume we are within the collision regime where the binary approximation is valid. This is accounted for in the model by including it in the calculation of the susceptibility for single transitions, replacing $\Gamma_0$ in Eq. (5) with $\Gamma_{tot}$, where $\Gamma_{tot} = \Gamma_0 + \Gamma_{col}$. The line shape is then summed over all transitions to generate a spectrum describing the natural line shape broadened by interatomic collisions.

The extreme narrowing is illustrated in Fig. 5(b), where the narrowed line shape (purple line) is compared to the Doppler broadened absorption spectrum expected for longer cell lengths (gray area). At low temperatures ($\lesssim 100$ °C), this narrowing can be so extreme that all individual hyperfine states can be resolved on the Rb $D_2$ line [see Fig. 2(a) in [20]]. The spectra taken in this experiment, e.g., that shown in Fig. 2(b) exhibit strong Dicke narrowing, indicating that our measurement method is predominantly sensitive to the slow atoms moving parallel to the cell walls.

The model accounts for such velocity effects using a phenomenological bimodal velocity distribution for the atomic velocities. This is a phenomenological model, first described in...
We test if this bimodal distribution is appropriate, Monte Carlo simulations of atomic trajectories to test the appropriateness of the Dicke narrowing model used in our fitting. Simulations are performed with no AS force present (blue lines) and including the effect of the AS force (dashed red lines). These are compared to the bimodal distribution used in our fitting procedure (thick black lines). In panel (a) the weighting of contributions to the shape for atomic positions inside the cell is shown. The gray dashed lines mark 10 nm from the cell walls, where the AS force starts to have a considerable effect on the atoms. Panel (b) shows the velocity distribution of atoms. The distribution used in our model (black line) is in reasonable agreement with the simulations for atoms unaffected by the AS force (blue line) and atoms which have been accelerated towards the walls (dashed red line). For comparison, the Maxwell-Boltzmann distribution expected in cm scale vapor cells is shown (dashed black line). (c) A comparison of the resulting line shapes from each velocity distribution for the Cs D1 line, with zero detuning as the resonance frequency of the Cs 6S1/2F_g = 4 → 6P1/2F_e = 3 transition. Experimental data points and their associated errors are shown as white points. The deviation of the expected line shape is within experimental error margins, justifying the simplification used in our line-shape model.

$w = 40 \text{ \mu m}$ is the $1/e^2$ diameter of the excitation laser beam used in the experiment and $L$ is the length of the nanocell. The atoms are randomly placed uniformly across a region which is four times larger than the interaction region ($4w \times 4w \times L$), to account for atoms transiting into the interaction region during the simulation. The atoms are given random velocities according to Maxwell-Boltzmann statistics, and their motion is simulated over a time ($1 \mu s$) which is large compared to the lifetime of the excited state. We do not include any other decay mechanisms. We neglect desorption events, so atoms that hit the walls or move out of the interaction region are lost. This is justified since desorption processes are expected to happen on time scales much longer than the interaction time [46].

The results of the simulation are shown in Fig. 6, where dashed red (blue) lines show the results of the model without (with) AS forces present. Panel (a) shows the position-dependent interaction times of atoms inside the cell. Panel (b) compares the MC simulated (blue line) velocity distribution of the atoms to the bimodal distribution used in the model (solid black line) and the Gaussian distribution expected for a Doppler-broadened medium (dotted black line). The bimodal distribution is a reasonable approximation to the continuous distribution predicted by the MC simulation. After the convolution with the homogeneous contribution to the linewidth (from collisional broadening, etc.), the difference in the full absorption line shape between the bimodal and...
MC velocity distributions is very small, as evidenced in Fig. 5(c), where the change between the line shapes from the phenomenological bimodal distribution (solid black line) and the continuous distribution (solid blue line) is well within the error margins of experimental data (white points), validating our use of the bimodal model.

In Fig. 4(d), we account for the AS interaction by calculating the position-dependent AS shift $\Delta_{AS}(r)$ across the entire cell length $L$:

$$\Delta_{AS} = -\left[\frac{C_{\alpha}}{r^2} + \frac{C_{\alpha}}{(L - r)^2}\right],$$

where $C_{\alpha}$ is a coupling coefficient describing the strength of the AS interaction, and $\alpha$ is an exponent describing the power law of the AS interaction. The two terms in Eq. (9) simply sum the AS interaction from both cell walls. Both $C_{\alpha}$ and $\alpha$ are used as floating fit parameters to determine the form of the AS power law. $\Delta_{AS}$ is then weighted by the position-dependent interaction times, shown in blue in Fig. 6(a). The result is an asymmetric line shape representing shifts across the entire cell weighted by interaction times. This line shape is then convolved with the Dicke narrowed line shape to give the final result of the fitting function. Note that the AS forces slightly modify the position and velocity distribution as shown by the MC simulation results in Fig. 6 (red dashed lines), but this is only significant for distances less than 10 nm.

Additional broadening effects that are not currently modeled are accounted for by adding an excess broadening parameter $\Gamma_{ex}$ into the fit. We suspect these additional broadenings may be caused by radiation trapping within the nanocell, a future avenue of investigation.

To summarize; the model takes the natural line shape and includes the well-known self-broadening and a fitted additional broadening $\Gamma_{ex}$. We then convolve the line shape with a phenomenological bimodal velocity distribution to account for Dicke narrowing, with a fitted parameter $a$ representing the strength of the contribution of traditional Maxwellian velocity classes. The last step is to convolve with a line shape generated using the AS interaction, fitting for the AS coefficient for the excited-state transition $C_{\alpha}^{5S_{1/2} \rightarrow 5P_{3/2}}$ and the exponent of the interaction $\alpha$.

IV. RESULTS AND DISCUSSION

A. Rubidium $D_2$ line

Unlike other experiments that map out the AS interaction using peak shift measurements, we choose to investigate the AS interaction by fitting a full line shape which is most sensitive to smaller AS distances. Spectra are taken over a length range $L = 40-250$ nm at temperatures $T = 125, 150, 175$, and $200$ °C. The relative ease of acquisition of spectra may be caused by radiation trapping within the nanocell, a future avenue of investigation.

A color map showing the length dependence of the AS induced shifts is shown in Fig. 7. Data are on the $^{85}$Rb $5S_{1/2}/F_g = 2$ line to the $^{85}$Rb $5P_{3/2}/F_e = 1, 2, 3$ excited state for $T = 150$ °C. The expected AS shift for $r_{max} = L/2$ is plotted as a white dashed line, using $\Delta_{AS} = -C_{\alpha}/(r_{max}^2)$. This data set clearly demonstrates the length dependence of the red tail caused by the AS interaction. However, in Rb, the red tail and shifts are not appreciable until cell lengths shorter than 80 nm, i.e., maximum AS separations of 40 nm. Hence, fits performed will not be sensitive to the AS interaction outside of this length range.

At long lengths ($L > \lambda/4$), shifts due to the AS interaction on the ground-state transitions are very small—on the order of a few MHz. The impact on the line shape is minimal until shorter cell lengths. For the Rb $D_2$ line the asymmetric tail is not appreciable until cell lengths less than 80 nm as evidenced in Fig. 7. The asymmetric redshift characteristic of the AS interaction is not fully evident until the cell length is below 80 nm with maximum AS separation $r_{max} = 40$ nm. This means our fits are most effective in the length region $r_{max} = 10 - 40$ nm, where there is a sufficiently large red tail to fit to.

After background-count subtraction and normalization, spectra are fitted using the model outlined in the previous section. Examples of fit results on the Rb $D_2$ line for a temperature $T = 125$ °C are shown in Figs. 2(c) and 2(d). They show experimental spectra (black points) processed from the raw data shown in Figs. 2(a) and 2(b), fits performed for cell lengths of 60 nm (red line) and 250 nm (blue line).

FIG. 7. (Color online) An accumulation of many spectra for different cell lengths. Here we highlight the length dependence of the absorption spectra on the $^{85}$Rb $5S_{1/2}/F_g = 2$ line to the $^{85}$Rb $5P_{3/2}/F_e = 1, 2, 3$ excited-state transitions. The figure demonstrates a clear length dependence of the asymmetric red tail, as expected for the AS interaction. The expected AS shift for atoms in the center of the cell is plotted as a white dashed line. The actual peak shift does not follow exactly the expected $1/r^3$ form because the asymmetric red tail skews the peak location. Hence, line-shape fitting should be more effective than peak detection for determining the functional form of the AS potential.

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At long lengths ($L > \lambda/4$), shifts due to the AS interaction on the ground-state transitions are very small—on the order of a few MHz. The impact on the line shape is minimal until shorter cell lengths. For the Rb $D_2$ line the asymmetric tail is not appreciable until cell lengths less than 80 nm as evidenced in Fig. 7. The asymmetric redshift characteristic of the AS interaction is not fully evident until the cell length is below 80 nm with maximum AS separation $r_{max} = 40$ nm. This means our fits are most effective in the length region $r_{max} = 10 - 40$ nm, where there is a sufficiently large red tail to fit to.
(a) with an $\Upsilon$ of 0.1 indicates a possible overestimation of the errors involved in the fitting procedure [42]. However, as discussed earlier, this is caused by the large background counts for such a short cell length.

To extract an exponent $\alpha$, fit results from all spectra are taken, and an average weighted by the inverse of the $\Upsilon$ of the fit is calculated. The same treatment performed on fitted values of $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}}$ to determine the coupling coefficient. Ultimately we have determined the best values of $\alpha$ and $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}}$ to use in future fitting of absorption spectra. Using this method, we extracted a value of $\alpha = 3.02 \pm 0.06$, a value in good agreement with the theoretical expectation of $\alpha = 3.16$ for the ground-state interaction, discussed in Sec. III. We also find a value of $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}} = 1.4 \pm 0.3$ kHz $\mu m^3$, not in agreement with theoretical calculations of $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}} = 2.1$ kHz $\mu m^3$ [47]. Quoted errors for all results are based on the standard deviation of the fit and do not exclude systematic effects. Deviation of the fitted coefficient from theoretical values will be discussed in the next section.

To test the robustness of our fits, we refitted spectra from our data set using a simulated annealing (SA) fitting algorithm [53] instead of the Marquardt-Levenberg (ML) method. The SA fitting algorithm was adapted from the code in [50] to use our model of the absorption spectra from Sec. III. To identify the best fit, the SA algorithm tries fit parameters and calculates a cost value, calculated as the absolute value of the deviation of the fitted coefficient from theoretical values will be discussed in the next section.

The length dependence of the $\Upsilon$ (blue points) of each ML fit with the corresponding fitted values of $\alpha$ (red points) are plotted in Figs. 9(a) and 9(b) respectively. In panel (b), the experimentally determined value is highlighted with a black dashed line, with the standard deviation plotted as gray dashed lines. Comparing with Fig. 8(c), where there is a range of $\alpha$ where the cost value is minimal, between $\alpha = 3.2$ and 2.9, we can see that the fitted $\alpha$ from the ML fitting method all lie within this length range, showing that the ML fit explored the whole region of lowest cost values of $\alpha$, and still returns final fit parameters clustered around our final quoted value of $\alpha$. In panel (a) the $\Upsilon$ of the fit is generally larger for longer cell lengths, where the AS shift is not appreciable. Fitted values of $\alpha$ and $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}}$ calculated at these longer lengths have very little bearing on the nature of the AS interaction, and a weighted average using $\Upsilon$ will decrease their impact on the estimated values. However, the larger uncertainty in best cost value for $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}}$ in the parameter space shows that this method is less suited to find an accurate value of $C_{\alpha}^{S_{5}^{0} \rightarrow S_{5}^{1}}$.

![FIG. 8. (Color online) Analysis of simulated annealing (SA) fits for a cell of length 80 nm, temperature 125°C.](image)
The final value of $\alpha = 3.02 \pm 0.06$ is plotted as a dashed black line, with the error bars plotted as beige dashed lines.

final measured value. For shorter cell lengths $L < 80$ nm, the AS interactions have much stronger effects on the line shape also coinciding with smaller values of $\chi$, with most fitted values of $\alpha$ in good agreement with the final average value and its associated errors.

**B. Cesium $D_1$ line**

To corroborate the results found in Rb, and to test the model with other alkali-metal atoms, the experiment was performed in a Cs NC on the Cs $D_1$ 894-nm line, with large hyperfine splittings (9 GHz for the Cs ground states and 1.2 GHz on the excited states). Each hyperfine transition is separated such that it can be considered in isolation from all others, even in the presence of a large AS interaction. This allows the reliable measurement of shifts with a precision of a few MHz.

While the ability to address individual transitions gives exceptionally high resolution, the technical challenges of the Cs $D_1$ line are greater than the Rb $D_2$ line, primarily due to the transition wavelength. First, the quantum efficiency of Si, used for detection in the SPCMs, is much lower at 894 nm than at 780 nm and hence the detectors are not as sensitive. Second, high transmission, narrow bandpass filters are currently not available at 894 nm meaning relatively more thermal background photons (of which there are more in absolute number compared to 780 nm) reach the detector. As a result of these two factors, we limit our investigation to nanocell thicknesses greater than 100 nm for the Cs $D_1$ line in order to generate spectra with sufficiently high signal-to-background ratio.

Using the same methods as those to extract parameters for Rb, we find a value of $C_3^{6S_{1/2}\rightarrow6P_{1/2}} = (1.9 \pm 0.1)$ kHz $\mu m^3$, a value that, similar to the Rb coefficient, is in disagreement with theoretical expectations of $C_3^{6S_{1/2}\rightarrow6P_{1/2}} = 1$ kHz $\mu m^3$.

In Fig. 10, we present a comparison of the red and blue wings of AS shifted transitions, the Cs $6S_{1/2}F_s = 3 \rightarrow 6P_{1/2}F_r = 4$ transition. Zero detuning is the resonance frequency of the line. There is a remarkable difference between the two wings, showing what a profound impact the AS interaction has on the line shape. The data (black points) are compared to the red wing as fitted by our model [dashed red line, mirrored in panel (b) for comparative purposes] and a Lorentzian fit to the blue wing (blue line). A Lorentzian fit is sufficient to model the blue wing, because Doppler broadening is suppressed by Dicke narrowing of the resonance.

Additional physical effects occurring in the cell not included in our simplified model are fitted as a phenomenological excess Lorentzian broadening $\Gamma_{ex}$. Although this excess broadening does not account for all physical effects occurring inside the cell, it can be seen from Fig. 10(b) that it is sufficient in describing the line shape in the absence of any AS effects. In this excitation scheme AS induced shifts are exclusively a redshift, as evidenced in Fig. 10(a). Hence, if the model can sufficiently describe the line shape, the simplification of using $\Gamma_{ex}$ is justified.

**V. CONCLUSION**

We measure and analyze the resonance line shapes of atoms confined between sapphire plates with separations between 30 and 250 nm. The line shapes are asymmetric due to the AS interaction. We fit the absorption line shapes in this length range, with an AS interaction of the general form $-C_{\alpha}/r^\alpha$. We found the best fitted values by fitting absorption spectra taken at multiple temperatures over the aforementioned length ranges, a method.
that greatly enhances the precision of our experiment. The resulting fitted parameters were averaged with a weighting according to the reduced $\chi^2$ squared (denoted as $\chi^\gamma$) of the fit. We find an averaged value of $\alpha = 3.02 \pm 0.06$, a value in good agreement with theoretical expectations for the atom-surface interaction inside the near field, and confirmed by other experiments [55].

We also found a fitted value of $C_{55_{1/2}\rightarrow5P_{1/2}} = 1.4 \pm 0.1$ kHz $\mu$m$^3$, a value not in agreement with theoretical expectations of 2.1 kHz $\mu$m$^3$. We postulate that the discrepancy between experiment and theory may be caused by rubidium adsorbed on the interior surface of the cell, interfering with the surface permittivity and therefore the reflection coefficient used to calculate $C_{3_{55_{1/2}\rightarrow5P_{1/2}}}$ [28,45]. The effect of metallic layers on the surface affects only the $C_{3_{55_{1/2}\rightarrow5P_{1/2}}}$ coefficient, leaving the exponent of $r^8$ unchanged [45]. This leads us to conclude that vapor cells may not be an appropriate medium for the accurate measurement of $C_3$ without rigorous theoretical treatment to account for the effects of surface atoms, currently beyond the scope of this experiment. There may be more complex interactions occurring inside the cell [34], such as additional motional effects between photon absorption and fluorescence, multiple reflections, and surface charges. However, we have demonstrated that a simple model is sufficient to describe the power law of $1/r^3$ for spectra over the length scales investigated. Furthermore, the effects of surface roughness [34] (on the order of 3 nm in both cells) are not a concern for our measurements. Atoms travel inside the cell at rms velocities exceeding 200 m/s, meaning atoms experience the surface roughness as a time averaged potential. Therefore at the distance ranges probed by this experiment, the AS separation can be considered to be well defined.

In the future we intend to utilize the methods developed herein to aid future investigations on the AS interaction, including the search for bound states close to the surface [56], and investigate higher-excited D states [17]. To further characterize our system, we also hope to look at the effects of radiation trapping [57]. Finally, we will use the model developed to aid in the fabrication and testing of nanocells being developed in Durham. The data presented in this paper is available online [58].

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