

A Comprehensive Study of the Bound States of Strontium Dimers on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ Potential

Senior Thesis

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Abstract

A Comprehensive Study of the Bound States of Strontium Dimers on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ Potential

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This thesis provides a comprehensive analysis of the bound states of homonuclear strontium dimers, for all of its naturally-occurring isotopes, on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ potential. The binding energies for nine new bound states of ^{88}Sr are measured using photoassociative spectroscopy and reported. These measurements, along with recent measurements for ^{84}Sr , ^{86}Sr , and ^{87}Sr , are used to do a combined fit to the semiclassical LeRoy-Bernstein equation. This allows for a combined analysis of the long-range part of the potential and enables predictions for the binding energies of other weakly-bound states. Furthermore, from this analysis, the value of the 1P_1 atomic state lifetime is determined to be $\tau = 5.20 \pm 0.02\text{ ns}$, which is consistent with previously determined values of the 1P_1 atomic state lifetime.

The spectroscopic data of all four strontium isotopes is also used to fit the parameters of a modified Lennard-Jones potential that provides a computationally complete picture of the $^1S_0-^1P_1$ potential. This modified Lennard-Jones potential is of the form $V(r) = \sigma/r^{12} - C_3/r^3$, where the potential parameters σ and C_3 were determined using a least squares fit, yielding an optimal value of $C_3 = 74.68\text{ eV \AA}^{-3}$. Due to the computational limitations, the value of σ was indeterminate. From the value of the long-range dispersion coefficient C_3 , the value of the 1P_1 atomic state lifetime is calculated to be $\tau = 5.21\text{ ns}$, which is consistent with the τ determined from LeRoy-Bernstein analysis.

The results of this thesis are expected to assist with further ultracold atomic physics experiments using strontium.

Acknowledgements

This is where I will write my acknowledgements.

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1 Introduction

Ultracold gases of the various isotopes of strontium serve as ideal model systems because the individual particles and their interactions are well-characterized, and in some cases, their interactions can be precisely controlled. Hence, they are currently studied for a wide range of applications, including optical frequency metrology, quantum simulation of many-body physics, the study of Rydberg physics, and the study of cold collisions. The fermionic isotope ^{87}Sr is of particular note due to its applications in creating precise optical atomic clocks. In many of these experiments, ultracold samples of strontium are trapped in optical lattices in order to prevent atom-atom interactions and introduce spatial periodicities. Photoassociative spectroscopy, which involves studying the optical formation of a bound molecular state from two initially free atoms, is a powerful and well-established technique used for probing ultracold gases in optical lattices. Investigating the binding energies of strontium can provide further insight into the underlying molecular potentials, which can then inform the design of experiments using photoassociation to further probe quantum gases in optical lattices of strontium. Another specific example is that the knowledge of the molecular potential and the associated binding energies enables us to further specify the systematics of atomic clocks. At a more fundamental level, getting an understanding of the underlying molecular potentials, and comparing measurements with theory, tests our ability to calculate molecular binding energies, which is essential for ultracold atomic physics experiments.

Most previous spectroscopic studies of strontium have been performed with the bosonic isotopes, ^{84}Sr , ^{86}Sr , ^{88}Sr [8, 9, 12]. In past studies of ^{88}Sr dimers on the $^1\text{S}_0-^1\text{P}_1$ potential, fit parameters to the semiclassical LeRoy-Bernstein equation, which analytically describes the binding energies of weakly-bound vibrational states as a function of the vibrational quantum number, have been reported [12]. However, a comprehensive study of this particular molecular potential for all four isotopes of strontium dimers has not been done before. Recently, the first study of photoassociation on the fermionic isotope ^{87}Sr has been published by the Killian group [4], which included a combined LeRoy-Bernstein fit using spectroscopic

data for ^{84}Sr , ^{86}Sr , and ^{87}Sr that forms a component of this thesis. The combined LeRoy-Bernstein fit is extended in this thesis to include newly-measured binding energies of ^{88}Sr .

Furthermore, significant work has been done on determining the functional form and parameters of the strontium ground state molecular potential. However, no study of a general potential describing the $^1\text{S}_0$ – $^1\text{P}_1$ strontium molecular potential has been reported, and thus, this is a focus of my thesis. A general Lennard-Jones potential describing all the isotopes of strontium is expected to assist with further ultracold atomic physics experiments.

1.1 Description of the Potential

This thesis focuses on the $5s^2\ ^1\text{S}_0 + 5s5p\ ^1\text{P}_1$ potential. We start with two homonuclear strontium atoms in their ground state ($^1\text{S}_0 + ^1\text{S}_0$), near the dissociation limit, D , with a large internuclear separation, r . The attraction between the two atoms is predominantly described by the attractive van der Waal’s force, which has a potential of the form $V(r) = D - C_6/r^6$, where C_6 is a dispersion coefficient. A visualization of this potential is given by the blue curve in Fig. 1.1. A single photon that is red-detuned to the $^1\text{S}_0$ – $^1\text{P}_1$ atomic resonance can excite a single atom in the pair to the $^1\text{P}_1$ state, resulting in a $^1\text{S}_0 + ^1\text{P}_1$ bound state (this is the process of single-photon photoassociation). In the long-range, the van der Waal’s force is now dominated by the existence of a dipole-dipole interaction, and the long-range potential between the atoms in the $^1\text{S}_0 + ^1\text{P}_1$ dimer can be approximated as:

$$V(r) = D - \frac{C_3}{r^3} + \frac{\hbar^2[J(J+1)+2]}{2\mu r^2} \quad (1.1)$$

where μ is the reduced mass of the dimer, and C_3 is the long-range dispersion coefficient. Neglecting nuclear spin, note that an atom’s state is given by the $^{2S+1}L_J$ notation, where S is the electronic spin, L is the electronic orbital angular momentum, and J is the total angular momentum. In the ground state, $S = J = 0$, and because of selection rules, the molecular excited state is restricted to $J = 1$. The rotational energy is small and so the rotational

term in Eq. 1.1 can be neglected. This excited-state potential is shown by the orange curve in Fig. 1.1. The total number of vibrational bound states on this potential is estimated to be 350 ± 50 [11], and are numbered using the vibrational quantum number, ν , such that $\nu = 1$ corresponds to the most weakly-bound state and subsequent values correspond to more deeply-bound states.

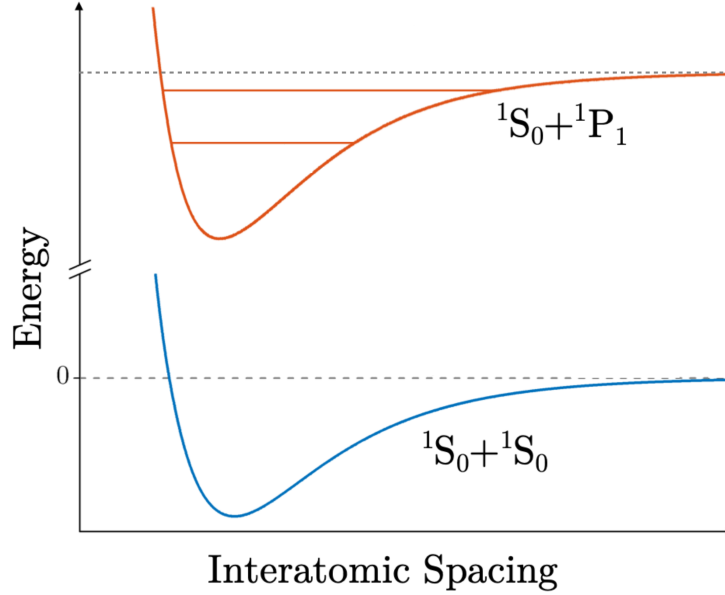


Figure 1.1: The potentials of relevance to this thesis: the initial potential between the ground-state strontium atoms (blue), and the excited-state molecular potential (orange), which is the subject of this thesis. The orange rungs in the $^1S_0-^1P_1$ potential represent bound states.

1.2 Thesis Overview

The subject of this thesis is to provide a fully comprehensive analysis of the binding energies of strontium dimers, for all of its naturally-occurring isotopes, on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ potential. In chapter 2, photoassociative spectroscopy of ^{88}Sr is described, and nine new spectroscopic lines are reported. In chapter 3, these measurements taken for ^{88}Sr are combined with spectroscopic measurements taken for ^{84}Sr , ^{86}Sr , and ^{87}Sr in [4] in a combined fit of the binding energies of all four strontium isotopes to the LeRoy-Bernstein equation, from which a value for the excited-state lifetime is extracted. Also using the spectroscopic measurements of all four strontium isotopes, chapter 4 reports on the computation of a

general Lennard-Jones potential that describes all the data. Finally, chapter 5 provides some concluding remarks, and suggestions for future studies. Note that because a component of the work done for this thesis was used in [4], a copy of the paper is included in appendix B for reference.

2 Photoassociative Spectroscopy

As briefly discussed in the introduction, photoassociative spectroscopy (PAS) is a powerful technique that in trapped laser-cooled gases can probe molecular potentials and provide an accurate determination of atomic state lifetimes. Photoassociation is the process by which one or more resonant laser fields illuminates an ultracold trapped gas of interacting atoms that can lead to the association of two initially free atoms to form a bound molecular excited state. As shown in Fig. 2.1, this is a resonant process — when viewed in the center-of-mass

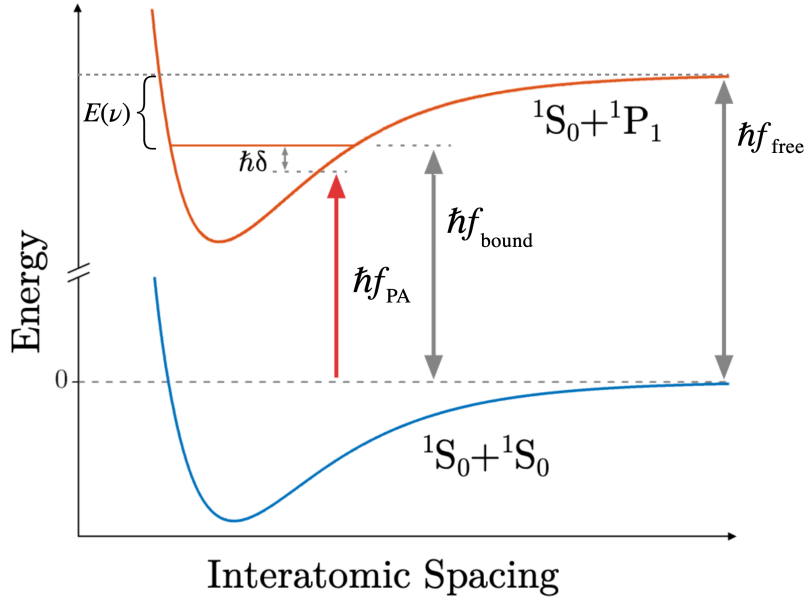


Figure 2.1: The photoassociation process. Figure adapted from [1].

frame of the two atoms, the sum of the initial kinetic energies of the two atoms involved and the energy of the absorbed photon ($\hbar f_{\text{bound}}$ in Fig. 2.1) add up to the energy of the bound state in the excited-state potential (in this case the $^1S_0 - ^1P_1$ potential). This process results in atom loss from the trap, which can happen in three ways: firstly, the formed $^1S_0 + ^1P_1$ dimer can simply escape the trap as it is no longer resonant with the trap's laser frequency; the $^1S_0 + ^1P_1$ dimer can decay and both atoms escape the trap with greatly increased kinetic energy (in other words, energy greater than the trap depth); the $^1S_0 + ^1P_1$ dimer can decay and the atoms can collide with other ground-state atoms, thus knocking them out of the

trap. Hence, trap loss is seen as evidence of photoassociation. PAS involves scanning the laser frequency (incrementally adjusting the PA laser frequency, f_{PA}), and measuring atom number at each frequency. Frequencies at which peak atom loss is observed are resonant frequencies — these allow us to determine the binding energies of the bound states. These binding energies, $E(\nu)$, are reported red-detuned from the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic resonance, and are given by $\hbar(f_{\text{free}} - f_{\text{bound}})$. In this work, $E(\nu)$ are reported as positive numbers in GHz.

Thus far, PAS has been used by the Killian group to measure the binding energies of all four isotopes of strontium, where the most recent measurements were taken for ^{84}Sr , ^{86}Sr , and ^{87}Sr in [4]. While PAS for ^{88}Sr has been performed by the Killian group previously, measuring the binding energies was not the focus of that work [9]. In addition, with further refinements having been made to the apparatus to take measurements for [4], my objective here is to use PAS to measure the binding energies of ^{88}Sr for previously unreported lines on the $^1\text{S}_0$ – $^1\text{P}_1$ potential.

2.1 Experimental Procedure

For the PAS of ^{88}Sr done as a part of this thesis, the experimental procedure is akin to that described in section II of [4]. Ultracold strontium atoms were first trapped in an optical dipole trap and photoassociation was performed after a short evaporation stage. For ^{88}Sr , the baseline number of trapped atoms was $\sim 2 \times 10^6$, which resulted in a typical atom density of $\sim 1 \times 10^{13} \text{ cm}^{-3}$. As noted in the previous section, atom loss from the trap is seen as evidence of photoassociation — peak atom loss due to photoassociation was observed to be 15 – 40%.

For each transition line, the PA laser frequency was fixed to a setpoint in the vicinity of the predicted value¹. The frequency of the PA laser is adjusted by detuning the frequency from the setpoint — denoted as Δf_{set} in this discussion. For each Δf_{set} , a measurement of

¹ Initial predictions of binding energies were computed using LeRoy-Bernstein analysis from previous spectroscopic data presented in Fig. 2b of [9]. LeRoy-Bernstein analysis for data-taking is described in more detail in chapter 3.1.

the PA laser energy was taken on the Exfo WA-1500 wavemeter in units of spectroscopic wavenumbers ($\tilde{\nu} = 1/\lambda$, units: cm^{-3}). A simplified schematic is shown in Fig. 2.2. The wavemeter is calibrated against the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic resonance.

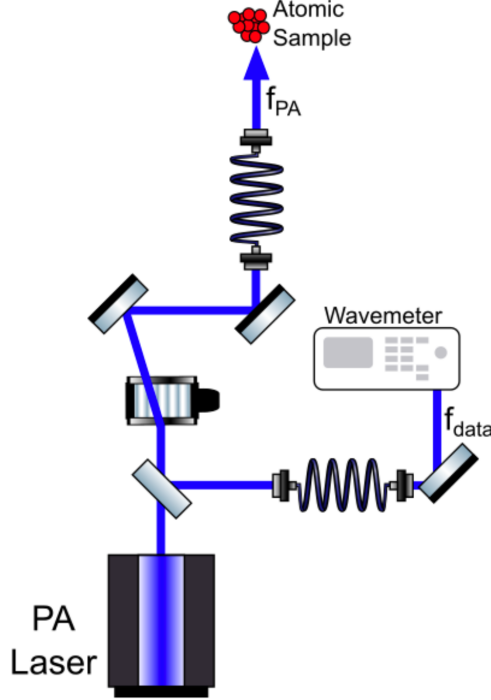


Figure 2.2: Simplified schematic of the experimental setup adapted from [3]. The PA laser is fixed to a setpoint, and adjusted by changing the detuning from the setpoint. The PA laser is split, with one ray going to the atomic sample, and another ray going to the Exfo WA-1500 wavemeter. Thus, for every Δf_{set} , we have a measurement of $\tilde{\nu}$.

For each transition line, between 3-7 scans across the predicted value were done. Since the PA laser energy is slightly different for each scan due to drifts, the mean and standard error of $\tilde{\nu}$ over all scans for each Δf_{set} was calculated. In order to convert between Δf_{set} and $\tilde{\nu}$, a linear interpolation of Δf_{set} and average $\tilde{\nu}$ is done, an example for which is shown in Fig. 2.3.

Measurements of atom number were taken with resonant time-of-flight absorption imaging [4], for each Δf_{set} . Each measurement of atom number for a particular Δf_{set} requires a new atomic sample to be prepared. For each transition line, the mean and standard error over all scans of atom number was calculated, and was fit to a Lorentzian lineshape to extract

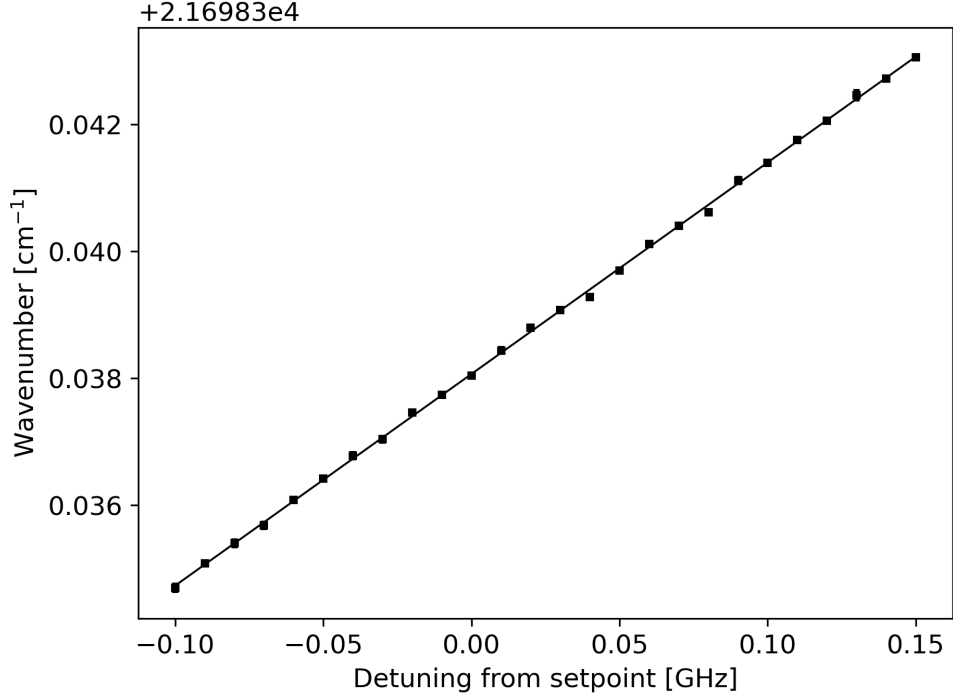


Figure 2.3: An example fit of the wavemeter reading against the detuning from setpoint. Using this linear interpolation, we can convert between Δf_{set} and $\tilde{\nu}$ for a particular transition line. This particular fit is for the measured $\nu = 68$ bound state (see Table 2.1).

the center frequency. Note that the atom loss is affected by both the molecular resonances and off-resonance atomic excitations, hence, we see a general decline in atom loss as we scan closer to the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic resonance. This is implemented as a linear background added on to the Lorentzian lineshape:

$$N = \frac{c_1}{\pi} \frac{\frac{1}{2}c_2}{(x - c_3)^2 + (\frac{1}{2}c_2)^2} + c_4x + c_5 \quad (2.1)$$

where N is the number of atoms, c_1 is the amplitude, c_2 is the full-width half-max of the lineshape, c_3 is the linecenter, c_4 is the linear background gradient, and c_5 is the linear background intercept. The extracted value of c_3 , and its corresponding standard error, are taken as the value and uncertainty of the binding energy in units of Δf_{set} — this is converted to units of $\tilde{\nu}$ using the linear interpolation described in Fig. 2.3. Finally, we can report the binding energies in terms of detuning from the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic resonance by using the

equation²:

$$E(\nu) = \hbar c (\tilde{\nu}_{\text{free}} - \tilde{\nu}_{c_3}) \quad (2.2)$$

where c is the speed of light in cm s^{-1} , $\tilde{\nu}_{\text{free}}$ is the wavenumber (in cm^{-1}) corresponding to the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic transition, and $\tilde{\nu}_{c_3}$ is the wavenumber (in cm^{-1}) corresponding to the linecenter, c_3 , extracted from Eq. 2.1.

2.2 Binding Energies of ^{88}Sr on the $^1\text{S}_0$ – $^1\text{P}_1$ Potential

We start by measuring the energy corresponding to the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic transition since it is necessary for calibrating the wavemeter and reporting the binding energies of ^{88}Sr dimers as given in Eq. 2.2. Using the most accurate reported value for the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ atomic transition of $21\,698.452 \pm 0.004 \text{ cm}^{-3}$ [10], we calibrated the reading of the laser energy correspondingly. Fig. 2.4 shows the atom loss against wavenumber for this measurement.

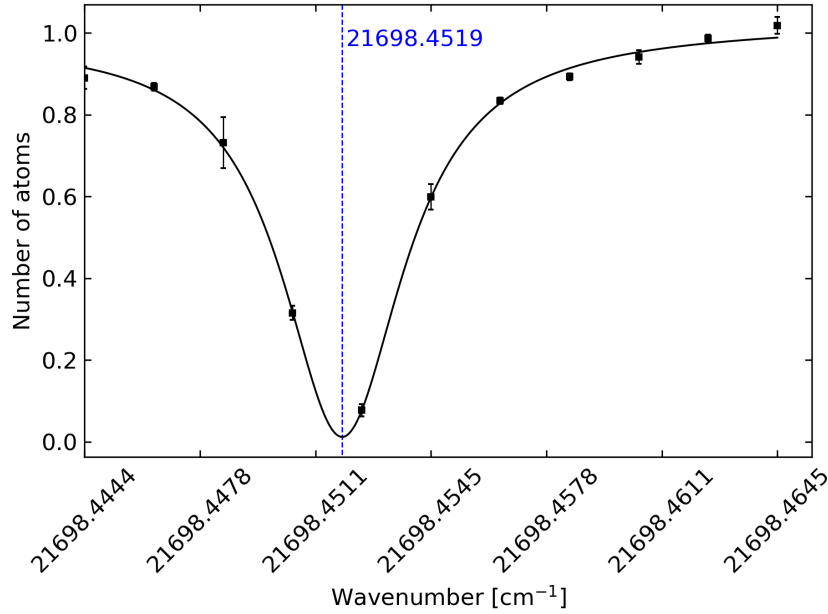


Figure 2.4: Measurement of the atomic resonance. Note that the peak atom loss is 100% since all atoms in the trap were ejected from the trap due to scattering photons.

² Note that the vibrational quantum number, ν , and spectroscopic wavenumbers, $\tilde{\nu}$, are unrelated, distinct quantities — the repetition of the Greek letter ‘ ν ’ is an unfortunate result of conventional notation.

In this work, we measure and report the binding energies of subsequent states as presented in Fig. 2 of [9]. Specifically, we identify nine previously unreported PAS lines, which are presented in Table 2.1. In order to better constrain the fit to the LeRoy-Bernstein equation, which is done in the next chapter, data was specifically taken for larger detunings in the range of $\sim 15 - 20$ GHz as well (the final three rows in Table 2.1).

Table 2.1: Measured binding energies of ^{88}Sr on the $5s^2\ ^1\text{S}_0 + 5s5p\ ^1\text{P}_1$ potential. σ_E are the propagated uncertainties of $E(\nu)$.

ν	$E(\nu)$ [GHz]	σ_E [GHz]
65	2.581	0.004
66	2.823	0.006
67	3.076	0.004
68	3.371	0.004
69	3.682	0.004
71	4.357	0.006
89	16.944	0.004
90	18.083	0.005
92	20.633	0.004

Fig. 2.5 shows the representative atom-loss spectra for the more weakly-bound states measured (the first six rows in Table 2.1). Furthermore, Fig. 2.6 shows two example fits of data to Eq. 2.1 for $\nu = 66$ and $\nu = 89$.

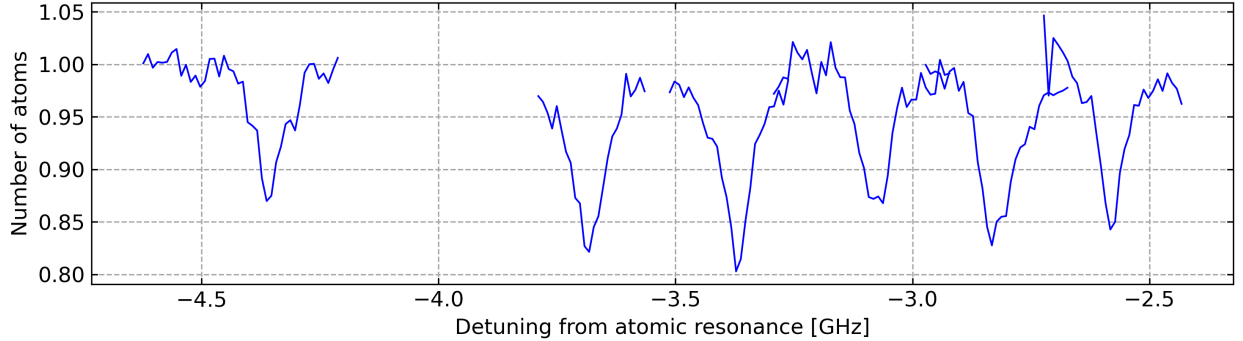
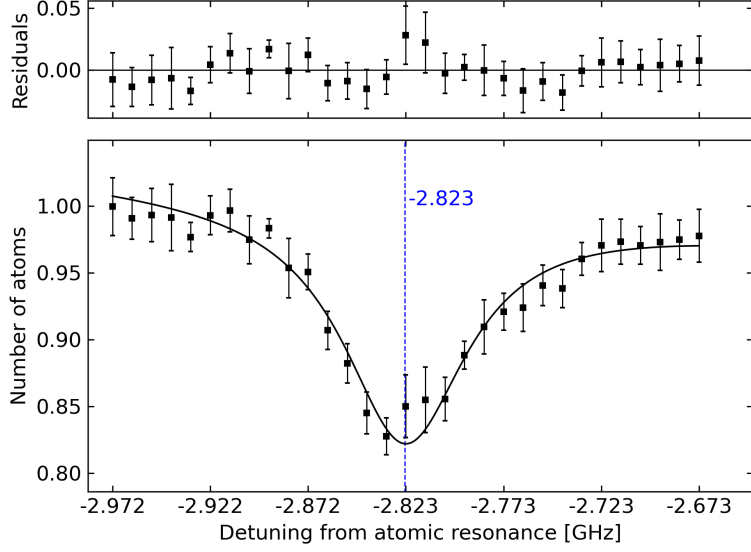
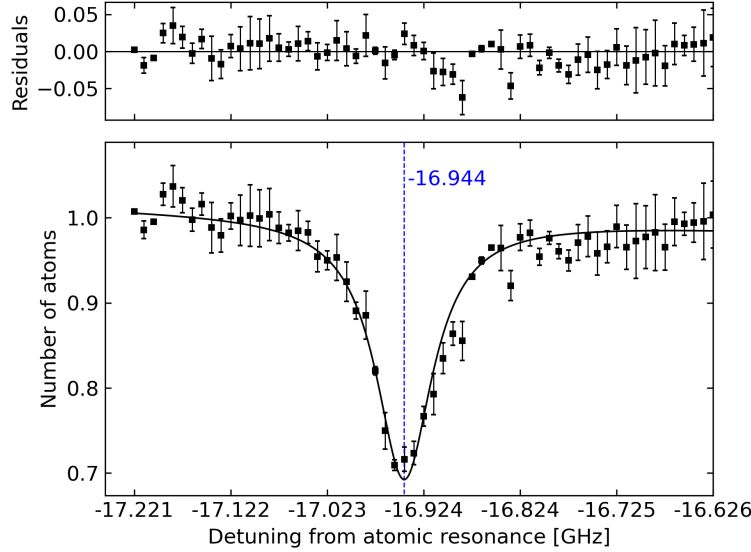


Figure 2.5: Representative atom-loss spectra. Lines connect the data points to guide the eye. The background atom number for each line is individually normalized to be one.



(a) Weaker bound state ($\nu = 66$).



(b) More deeply bound state ($\nu = 89$).

Figure 2.6: Example fits of data to Eq. 2.1 for (a) a more weakly-bound state ($\nu = 66$), (b) a more deeply-bound state ($\nu = 89$). The atom number is individually normalized for each transition line such that the value of the linear background at the linecenter is taken to be one. In both plots, we see a linear background that decreases for detunings closer to the atomic resonance, with a more pronounced effect visible in (a), as expected.

Ultimately, in this section, we have reported nine new measured binding energies of ^{88}Sr on the $^1\text{S}_0$ – $^1\text{P}_1$ potential using PAS. Combining this data with existing PAS data from [4], we can perform analysis of the binding energies and the underlying molecular potential.

3 LeRoy-Bernstein Analysis

Having taken spectroscopic data for all four isotopes of strontium, it is now possible to find a general model that describes the binding energies of the bound states of strontium dimers. For a potential with a long-range form given by Eq. 1.1, and neglecting the rotational energy, a semiclassical treatment leads to the so-called LeRoy-Bernstein formula, shown in Eq. 3.1. This gives the binding energies, $E(\nu)$, of vibrational states close to the dissociation limit (or atomic resonance), D , as a function of vibrational quantum number [7].

$$E(\nu) = D - [(\nu_D - \nu)H_3]^6, \quad H_3 = \frac{1}{C_3^{\frac{1}{3}}} \frac{\hbar \Gamma\left(\frac{4}{3}\right)}{2\Gamma\left(\frac{5}{6}\right)} \sqrt{\frac{2\pi}{\mu}}, \quad C_3 = \frac{3\hbar\lambda^3}{16\pi^3\tau} \quad (3.1)$$

Here: ν is the vibrational quantum number such that $\nu = 1$ corresponds to the most weakly-bound state; ν_D is an effective vibrational index between 0 and 1; Γ is the gamma function; μ is the reduced mass of the strontium dimer; λ is the wavelength corresponding to the $^1S_0 \rightarrow ^1P_1$ atomic transition, and is given by 460.86 nm [10]; τ is the $5s5p\ ^1P_1$ atomic state lifetime.

For our case, it is important to note that Eq. 3.1 is only valid for weakly-bound states, and does not hold for more deeply-bound states. Since our measurements are taken with respect to the atomic resonance such that D is set to zero, and the binding energies are quoted as positive numbers, the measurements from PAS are fit to the functional form:

$$E(\nu) = [(\nu_D - \nu)H_3]^6 \quad (3.2)$$

The objective here is to do a combined fit for all the isotopes of strontium to the LeRoy-Bernstein equation, where ‘combined’ specifically refers to the fact that spectroscopic data for all the isotopes is fit to the same C_3 coefficient, which results in the same value for the excited-state lifetime for all the isotopes. The ν_D values for each isotope are independently fit. The simplified LeRoy-Bernstein equation (Eq. 3.2) therefore describes the binding

energies of the weakly-bound molecular states for each strontium isotope as a function of the vibrational quantum number, from which a value for τ can be extracted. This fitting process was implemented in Python, using the `scipy.optimize.curve_fit` method which uses non-linear least squares to fit a function to data. It minimizes the chi-squared function

$$\chi^2 = \sum_i \frac{(M_i - F_i)^2}{\sigma_i^2} \quad (3.3)$$

where M_i are the spectroscopic measurements, σ_i are the uncertainties in the measurements, and F_i are the fit binding energies given by Eq. 3.2.

3.1 LeRoy-Bernstein Analysis During Data-taking

While the central objective of this chapter is to fit the spectroscopic data of all four strontium isotopes to the functional form in Eq. 3.2, which is the topic of the subsequent section, it is informative to take a quick detour and discuss three utilities of LeRoy-Bernstein analysis which was extremely useful during the data-taking process (both for the measurements taken in the previous chapter, as well as for [4]).

Firstly, for every round of spectroscopic data taken, the extracted binding energies were fit to the LeRoy-Bernstein equation. From this, τ was extracted and compared to values found from previous studies to check that appropriate values of binding energies were being measured [8, 9, 12]. Furthermore, fitting measurements also allowed us to check that appropriate values of ν_D were being obtained to make sure that the quantum numbers ν were being assigned to the bound levels properly. This was an ongoing process where fits were continuously done to new, incoming data.

Next, the fits also allowed us to generate predictions for binding energies for other bound states. As mentioned in chapter 2, the LeRoy-Bernstein fitting program was run periodically every time spectroscopic lines were found to allow for a more precise prediction of wavenumbers to scan for new lines. Since every instance of PAS for a particular wavenumber

requires a new sample of strontium atoms to be created, scanning a large range of wavenumbers with small increments can be time-consuming. Thus, predictions from LeRoy-Bernstein equation allowed for more focused data-taking, where we were able to scan a more precise range of wavenumbers with smaller increments to better determine the linecenter, and thus the binding energy.

Finally, fitting to Eq. 3.2 allowed for systematic/calibration errors in the apparatus to be identified. We found a better estimate for such errors by allowing for an extra fit parameter:

$$E(\nu) = [(\nu_D - \nu)H_3]^6 + K \quad (3.4)$$

where K is a binding energy offset. This was especially crucial in the first few rounds of data-taking in [4] as the K value was found to be on the order of several hundred megahertz, and the corresponding sources of the offset were identified and fixed.

3.2 Published Results from *Photoassociative Spectroscopy of ^{87}Sr*

As stated previously, a component of the work done for this chapter was included in the Killian lab’s paper on the *Photoassociative Spectroscopy of ^{87}Sr* [4]. This paper included a combined LeRoy-Bernstein fit of PAS data of ^{84}Sr , ^{86}Sr , and ^{87}Sr , and is presented in this section. The combined fit is shown in Fig. 3.1a with fit residuals for each isotope. Table 3.1 describes the fit parameters of this combined fit. Tables of observed binding energies of ^{84}Sr , ^{86}Sr , and ^{87}Sr are provided in appendix A for reference.

Table 3.1: Fit parameters for the combined fit of binding energies of ^{84}Sr , ^{86}Sr , ^{87}Sr to Eq. 3.2.

Isotope	ν_D	τ [ns]
^{84}Sr	0.872 ± 0.016	5.202 ± 0.002
^{86}Sr	0.203 ± 0.016	
^{87}Sr	0.866 ± 0.018	

An important point to note from the fit described in Table 3.1 is that although the

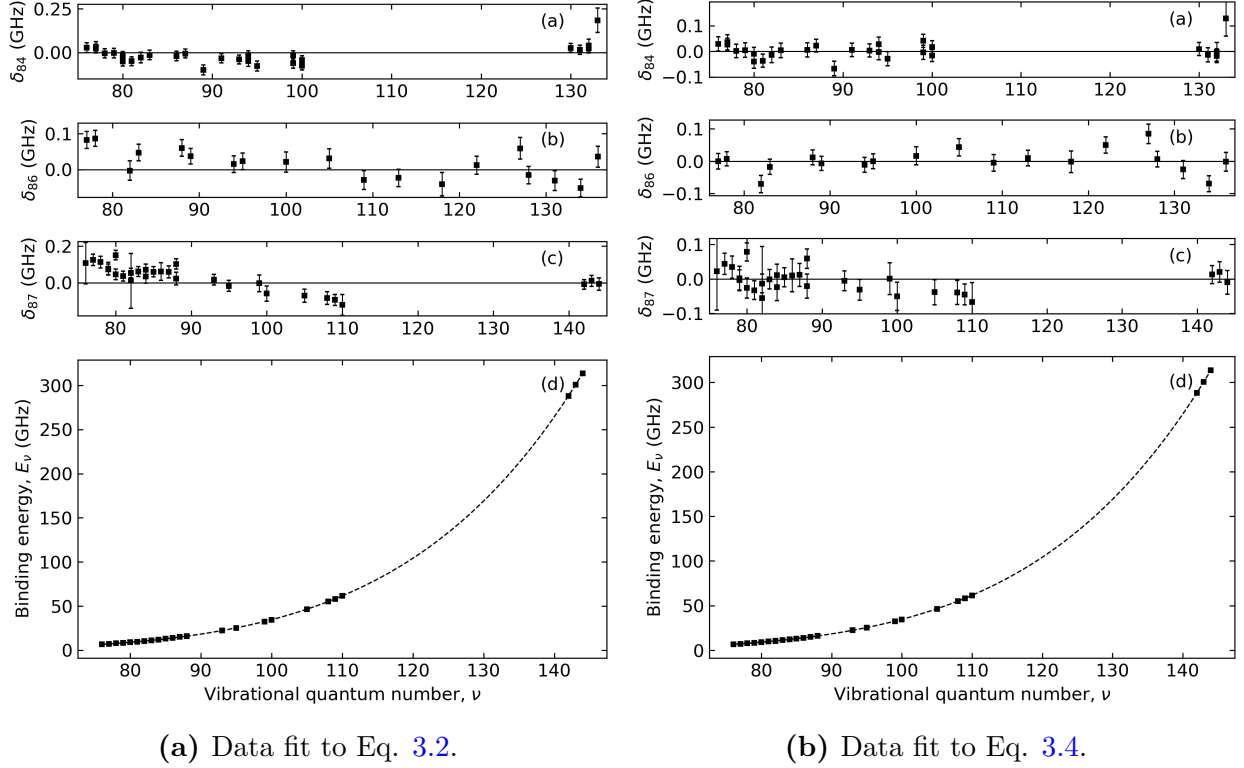


Figure 3.1: Fit of the binding energies of states on the $5s^2 \ ^1S_0 + 5s5p \ ^1P_1$ molecular potential for all four strontium isotopes. Plots (a-c) of both subfigures show the residuals of the fit for ^{84}Sr , ^{86}Sr , and ^{87}Sr , respectively. Plot (d) of both subfigures shows the measured binding energies of ^{87}Sr as a function of ν , where the dashed line is the best fit of the data to the corresponding model.

statistical uncertainty in τ is small (around 0.04%), we can see from Fig. 3.1a that the fit residuals shown in plots (b-c) show a systematic trend corresponding to ~ 100 MHz variation over a change of ~ 100 GHz in binding energy. This trend might indicate a systematic error in the measurement tool, such as the wavemeter accuracy degrading the further we get from the wavenumber at which it was calibrated. It may also be a result of variation in molecular-state AC Stark shifts from the optical dipole trap laser fields, or the influence of additional terms in the molecular potential not accounted for by the LeRoy-Bernstein formula. To determine a better estimate of the uncertainty in τ given in Table 3.1, we fit the data again, but this time to Eq. 3.4, allowing for each isotope to be fit to its own K . The values of K for each isotope are shown in Table 3.2, and the fit is shown in Fig. 3.1b.

From Table 3.2, we see that the binding energy offset for the ^{86}Sr and ^{87}Sr datasets is on

Table 3.2: Offsets for the combined fit of binding energies to Eq. 3.2 for ^{84}Sr , ^{86}Sr , and ^{87}Sr .

Isotope	Offset [GHz]
^{84}Sr	0.043 ± 0.013
^{86}Sr	0.137 ± 0.015
^{87}Sr	0.139 ± 0.014

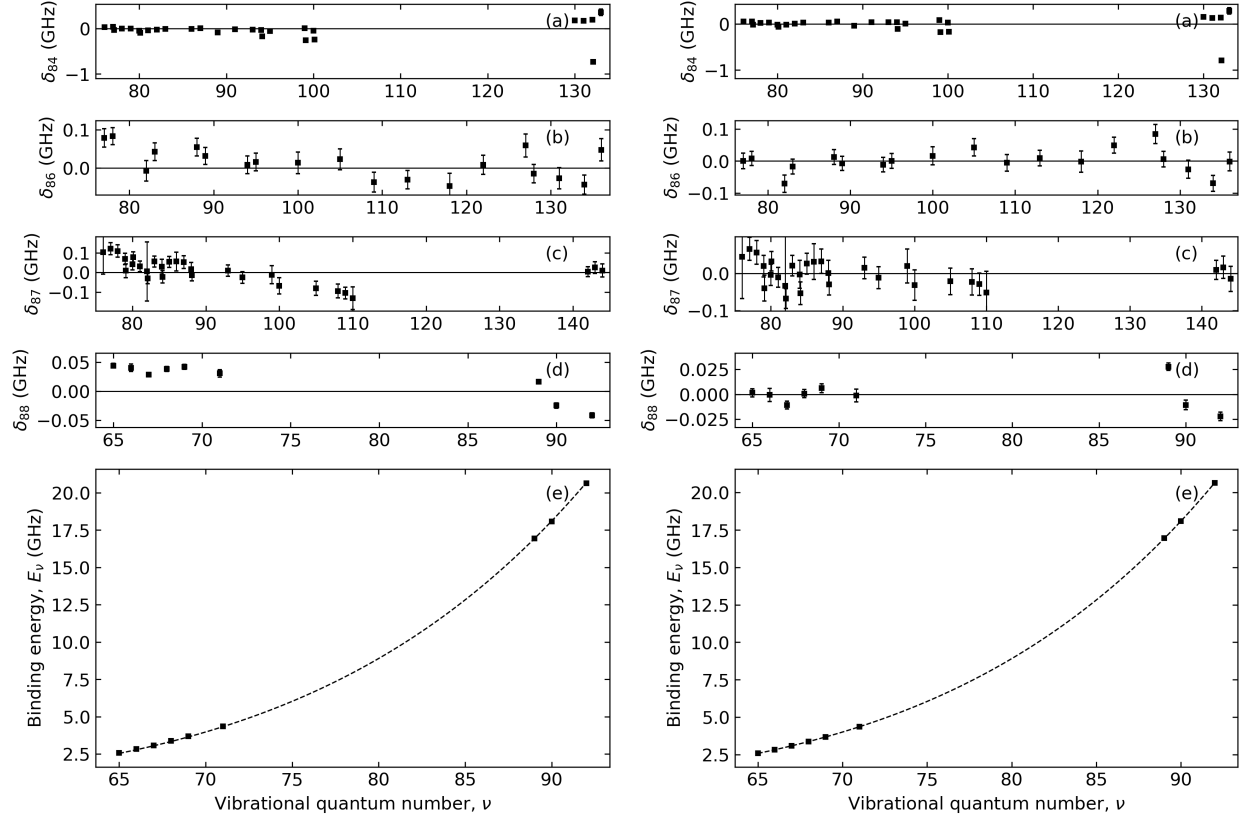
the order of ~ 140 MHz, whereas for ^{84}Sr it is on the order of ~ 40 MHz, which corroborates the trend observed in plots (a-c) of Fig. 3.1a. As we can see from the corresponding plots in Fig. 3.1b, fitting to Eq. 3.4 removed the systematic trends in the residuals. The extracted value of τ increased by 0.02 ns or 0.4%, which we take as our uncertainty. We thus quote our final value of the excited state lifetime as $\tau = 5.20 \pm 0.02$ ns. The value of τ determined here differs by 1% from the most accurate reported measurement of $\tau = 5.263 \pm 0.004$ ns, performed with photoassociation in an optical lattice [12], and is in closer agreement with a more recent value of $\tau = 5.234 \pm 0.008$ ns determined from AC Stark shifts of strontium levels [2].

3.3 Combined Fit of All Strontium Isotopes

Using the PAS data collected for ^{88}Sr in chapter 2, along with the PAS data for ^{84}Sr , ^{86}Sr , and ^{87}Sr from [4], we can achieve the central objective of this chapter: obtaining a LeRoy-Bernstein model for all four isotopes of strontium on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ molecular potential. The parameters for this combined fit are described in Table 3.3, and the plot is shown in Fig. 3.2a. A table of observed values, fit values, fit residuals, and RMSE of the fit is provided in appendix A for reference.

Table 3.3: Fit parameters of the combined fit of binding energies of all four isotopes to Eq. 3.2.

Isotope	ν_D	τ [ns]
^{84}Sr	0.874 ± 0.035	5.201 ± 0.004
^{86}Sr	0.187 ± 0.036	
^{87}Sr	0.850 ± 0.039	
^{88}Sr	0.493 ± 0.026	



(a) Data fit to Eq. 3.2.

(b) Data fit to Eq. 3.4.

Figure 3.2: Fit of the binding energies of states on the $5s^2 \ ^1S_0 + 5s5p \ ^1P_1$ molecular potential for all four strontium isotopes. Plots (a-d) of both subfigures show the residuals of the fit for ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr , respectively. Plot (e) of both subfigures shows the measured binding energies of ^{88}Sr as a function of ν , where the dashed line is the best fit of the data to the corresponding model.

Note that in plots (b-d) we observe the same systematic deviation in the fit residuals as seen in the previous section. As such, the same treatment is done, allowing for a binding energy offset to be fit individually for each isotope; the combined fit to Eq. 3.4 is shown in

Fig. 3.2b. Table 3.4 shows the value of K for each isotope.

Table 3.4: Offsets for the combined fit of binding energies to Eq. 3.4 for all four strontium isotopes.

Isotope	Offset [GHz]
^{84}Sr	0.029 ± 0.038
^{86}Sr	0.136 ± 0.045
^{87}Sr	0.115 ± 0.041
^{88}Sr	0.067 ± 0.010

We see that the offsets (incorporating uncertainties) for ^{84}Sr , ^{86}Sr , and ^{87}Sr in Table 3.3 are comparable to the corresponding offsets in Table 3.2, and the offset for ^{88}Sr is on the order of ~ 70 MHz. Although sources of systematic/calibration errors in the apparatus were identified and fixed in the preliminary stages of data-taking, as described at the end of section 3.1, it appears that there is some persistent systematic source of offset, the possible sources of which were identified in section 3.2. Furthermore, similar to the combined fit with offset shown in Fig. 3.1b in the previous section, the combined fit shown in Fig. 3.2b increased the extracted value of τ by 0.02 ns or 0.4%, which we take as our uncertainty. Thus, after incorporating the PAS data for ^{88}Sr , we find the same value of τ as in [4]:

$$\tau = 5.20 \pm 0.02 \text{ ns}$$

Ultimately, in this chapter, we have found a LeRoy-Bernstein model to describe the weakly-bound states of all four isotopes of strontium on the $5s^2 \ ^1S_0 + 5s5p \ ^1P_1$ potential. The LeRoy-Bernstein model in Eq. 3.2 with the ν_D and τ fit parameters described in Table 3.3 can be used to generate predictions for the binding energies of other weakly-bound states of strontium on this particular potential. However, as stated in [6], Eq. 3.1 is a semiclassical approximation and the predictions are valid for ranges of ν which were used to fit Eq. 3.4. For a more accurate determination of predicted binding energies and τ , a quantum mechanical integration of the molecular potential is required, which is the subject of the next chapter.

4 An Effective Lennard-Jones Potential

The second major computational component of this project is finding an effective potential to describe all the data. This will allow for specific binding energies and corresponding wavefunctions to be computed by solving the radial Schrödinger equation (Eq. 4.1).

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 u}{\partial r^2} + V(r)u + \frac{\hbar^2[J(J+1)+2]}{2\mu r^2} = Eu \quad (4.1)$$

As noted in chapter 1.1, only $J = 1$ states are excited, and the rotational term in Eq. 4.1 is negligible. We will use an approximate functional form for the potential in the form of a modified Lennard-Jones potential, given by:

$$V(r) = \frac{\sigma}{r^{12}} - \frac{C_3}{r^3} \quad (4.2)$$

where σ and C_3 are the parameters to find, and C_3 is the same parameter as denoted Eq. 3.1. The σ term controls the inner wall of the potential and the C_3 term controls the long-range behavior of the potential. Essentially, this potential can be put into the Schrödinger equation, and the eigenenergies, E , and corresponding eigenstates, u , can be solved for numerically. This provides a computationally complete picture of the strontium $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ molecular potential. While this thesis was not able to fully determine the potential's parameters, a simple computational method is provided for future work to build off of.

4.1 Fit Procedure

Thus far, significant work has been done in determining the functional form of the ground-state molecular potential — the codebase developed in [5] was used to compute an improved determination of the ground-state molecular potential, and a similar, simplified version of the fit procedure is used in this thesis. The procedure to compute the values of σ and C_3 will

be done by optimizing these parameters, where the binding energies of ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr measured from PAS will be compared to the solutions to the Schrödinger equation for the same states, and the parameters will be adjusted iteratively to minimize the difference between the calculated and measured results.

4.1.1 Description of the Numerical Method

In order to solve Eq. 4.1 numerically, we must rearrange and discretize the equation. The second derivative is approximated as a centered finite difference. The discretized version of Eq. 4.1 is given by:

$$\begin{aligned} & -\frac{\partial^2 u}{\partial r^2} + \frac{2\mu}{\hbar^2} V(r)u = \frac{2\mu}{\hbar^2} Eu \\ \Rightarrow & \frac{-u_{i-1} + 2u_i - u_{i+1}}{\delta^2} + \frac{2\mu}{\hbar^2} V_i u_i = \frac{2\mu}{\hbar^2} Eu_i \\ \Rightarrow & \frac{-u_{i-1}}{\delta^2} + \left(\frac{2}{\delta^2} + \frac{2\mu}{\hbar^2} V_i \right) u_i - \frac{u_{i+1}}{\delta^2} = \frac{2\mu}{\hbar^2} Eu_i \end{aligned} \quad (4.3)$$

where we use a grid of $N + 1$ equally-spaced radial coordinates r_i , $i = 0, \dots, N$, and the grid spacing is denoted by δ . For brevity, we define $u_i := u(r_i)$ and $V_i := V(r_i)$. We must also consider the boundary conditions, that is, what happens at u_0 and u_N . The actual wavefunctions, u , exponentially decay in the classically forbidden regions such that:

$$u(r \rightarrow \pm\infty) = 0 \quad (4.4)$$

For a numerical scheme, Eq. 4.4 can be approximated by the Dirichlet boundary conditions, $u_0 = u_N = 0$. It is necessary to extend the radial coordinate grid far enough into the classically forbidden regions for the Dirichlet boundary conditions to be sufficiently accurate approximations to Eq. 4.4. For the left boundary condition, due to the $1/r^{12}$ behavior of the potential in the short range, it is not necessary to extend far into the inner classically forbidden region before the wavefunction starts to decay sufficiently, and so $r_0 = 0.5 \text{ \AA}$ was found to be suitable.

Having discretized the equation, and having defined the endpoints of the grid, we can write Eq. 4.3 as a system of $N - 1$ linear equations in matrix form:

$$\begin{bmatrix} \left(\frac{2}{\delta^2} + \frac{2\mu}{\hbar^2}V_1\right) & -\frac{1}{\delta^2} & & 0 \\ & -\frac{1}{\delta^2} & \ddots & \\ & & \ddots & \ddots \\ & & & -\frac{1}{\delta^2} \\ 0 & & -\frac{1}{\delta^2} & \left(\frac{2}{\delta^2} + \frac{2\mu}{\hbar^2}V_{N-1}\right) \end{bmatrix} \begin{bmatrix} u_1 \\ \vdots \\ \vdots \\ u_{N-1} \end{bmatrix} = \frac{2\mu}{\hbar^2}E \begin{bmatrix} u_1 \\ \vdots \\ \vdots \\ u_{N-1} \end{bmatrix} \quad (4.5)$$

with $u_0 = u_N = 0$. Eq. 4.5 is a matrix-eigenvalue equation, where the eigenvalues are given by:

$$\lambda = \frac{2\mu}{\hbar^2}E \quad (4.6)$$

Thus, by finding the eigenvalues of the matrix in Eq. 4.5, we can rearrange Eq. 4.6 to find the eigenenergies of Eq. 4.1. There exists a plethora of optimized numerical linear algebra libraries in Python that can be used to solve for the eigenvalues in Eq. 4.5. Since the matrix we are concerned with is a symmetric tridiagonal matrix, we can employ the `scipy.linalg.eigvalsh_tridiagonal` routine which is specifically optimized to calculate the eigenvalues of such matrices. It is important to note that, depending on the number of grid points used, many more eigenvalues will be computed by this routine than there are physical bound states — these computed eigenvalues must be sorted to return the eigenvalues corresponding to physically valid states. Since a bound state cannot exceed the depth of the potential, $V_{\min}$, the routine is set to return eigenvalues between 0 and $2\mu|V_{\min}|/\hbar^2$.

4.1.2 Fitting Algorithm

A least squares fit can be done to optimize the parameters σ and C_3 in Eq. 4.2. First, the binding energies corresponding to the same vibrational quantum numbers as from the PAS data are found by numerically solving the Schrödinger equation (Eq. 4.5) using the

method outlined in the previous section. A comparison of the binding energies from the PAS data and numerical solutions is done using the following cost function:

$$F = \frac{1}{2} \sum_i (K_i - M_i)^2 \quad (4.7)$$

where K_i are the numerically calculated binding energies and M_i are the binding energies measured using PAS. The optimization of Eq. 4.7 is implemented in Python using the `scipy.optimize.least_squares` method, which terminates when a local minimum of the cost function is found.

4.2 Discussion of Method

As mentioned at the beginning of the chapter, the simple method discussed here yielded indeterminate results for the potential's parameters. While a benefit of the method outlined is that it is very straightforward, and thus easy to implement, a major drawback is its computational complexity. As the number of grid points is increased, the time complexity of the computation scales as $\sim N^3$. At the same time, without using a large number of grid points, it is difficult to resolve the deeply-bound states, which leads to an inaccurate computation of the eigenvalues in Eq. 4.6 and the corresponding eigenenergies.

A preliminary run of the fitting algorithm was done, with starting values of $\sigma = 0.5 \text{ eV } \text{\AA}^{-12}$ and $C_3 = 75 \text{ eV } \text{\AA}^{-3}$. The starting value of σ was chosen as it provided a large inner wall, and resulted in ~ 350 bound states between the values between 0 and $2\mu|V_{\min}|/\hbar^2$ for each isotope; the starting value of C_3 was chosen by using Eq. 3.1 with the value of the $^1\text{P}_1$ atomic state lifetime as determined from chapter 3. The least squares fit terminated at the same value of σ and an optimized value of $C_3 = 74.68 \text{ eV } \text{\AA}^{-3}$, which is equivalent to $\tau = 5.21 \text{ ns}$. This value falls within the uncertainty ranges of the derived value of τ from chapter 3.

However, when looking at the computed eigenenergies using these parameter values, it was found that for the more deeply-bound states, the residuals, compared to the observed

values from PAS, were extremely large. These residuals are shown in Fig. 4.1.

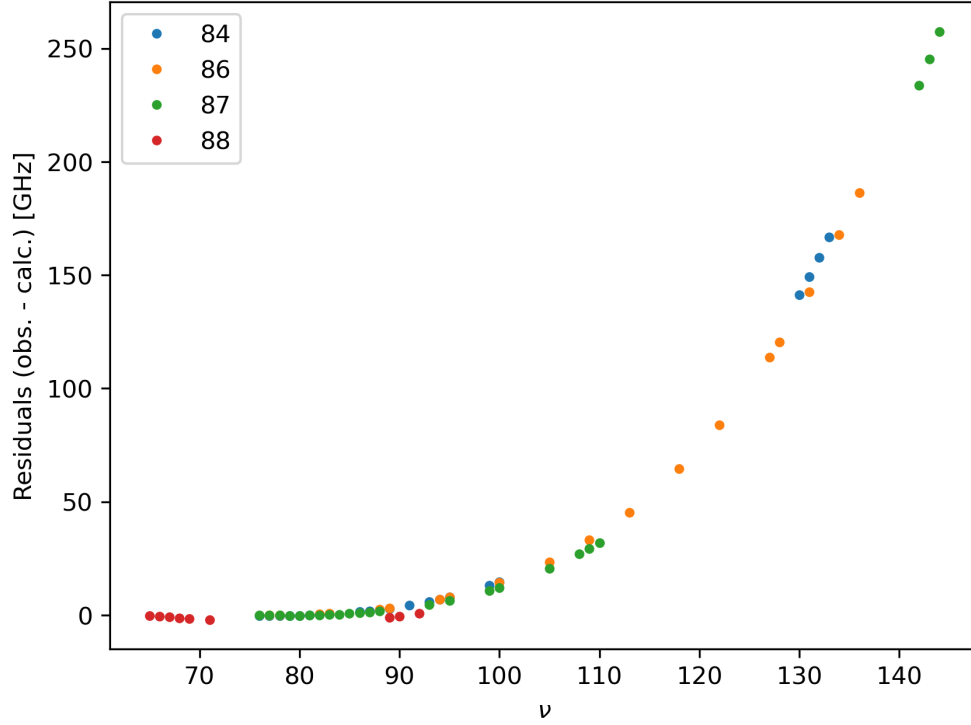


Figure 4.1: The residuals found when using the values $\sigma = 0.5 \text{ eV } \text{\AA}^{-12}$ and $C_3 = 74.68 \text{ eV } \text{\AA}^{-3}$. As more deeply bound states are considered, the values of the residuals explode. A similar trend is observed for all four isotopes.

Even though the least squares fitting algorithm terminated, a global minimum was not found, as indicated by the large residuals seen in Fig. 4.1. Therefore, adjustments to the numerical method discussed in this section need to be made in order to better determine the value of σ in the potential.

5 Conclusion

Ultimately, this thesis analyzes the bound states of homonuclear strontium dimers, for all of its naturally-occurring isotopes, on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ potential. The experimental work presented in chapter 2 illustrated the use of PAS as a powerful probe of molecular potentials, and nine new transition lines of ^{88}Sr were reported. Using these spectroscopic measurements, as well as those of ^{84}Sr , ^{86}Sr , ^{87}Sr from [4], a combined fit of the acquired PAS data to the semiclassical LeRoy-Bernstein equation was performed. From this analysis, a model for the weakly-bound states of all four strontium isotopes on the excited-state potential was derived, the parameters for which are presented in Table 3.3. Furthermore, from the combined fit, the 1P_1 atomic state lifetime was found to be $\tau = 5.20 \pm 0.02\text{ ns}$, which is within 1% of previously determined values of τ [2, 12].

As discussed at the end of chapter 3.2, there were potential sources of offset in the experimental apparatus. These offsets were different for each isotope, and are shown in Table 3.4. Future works should further investigate these sources of offset in order to better specify a model for the weakly-bound states of strontium dimers on the $^1S_0-^1P_1$ potential, and better determine a value for τ .

While a computational model to determine the parameters σ and C_3 was described, due to computational limitations, it returned an indeterminate value of σ , as discussed in chapter 4.2. For future studies with the aim of refining the values of the parameters σ and C_3 , further analysis into determining the most optimal hyperparameters (namely the right endpoint, and the number of grid points) should be done. Another remedy may be found in using a more robust computational method to solve the Schrödinger equation. The work done in [5] used the Johnson renormalized Numerov method which found success in refining the parameters of the strontium ground-state molecular potential — this codebase can be adapted for the deeper excited-state potential.

Although issues were encountered in the computation of an effective Lennard-Jones potential, the work in this thesis has nevertheless provided a more comprehensive understanding

of the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ molecular potential by performing a combined analysis of all four naturally-occurring strontium isotopes. The work done in this thesis illustrates the use of PAS to measure binding energies, which can be used to measure the binding energies of other weakly-bound states, and provides a starting point for future studies seeking to determine an effective Lennard-Jones potential that describes all the data.

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A Binding Energies for All Observed Transitions

The tables in this appendix contain binding energy observed values, fit values, fit residuals, and RMSE of the fits for all observed transitions, both from the PAS conducted for this thesis and for [4]. The fit values are obtained from a combined fit of all four strontium isotopes. Note that:

- E_{obs} refers to the observed binding energies from PAS, and σ_E is the uncertainty in the observed binding energy,
- $E_1(\nu)$ refers to the fit to Eq. 3.2, and δ_1 are the residuals corresponding to this fit,
- $E_2(\nu)$ refers to the fit to Eq. 3.4, δ_2 are the residuals corresponding to this fit,

In addition to the fit binding energies, the parameters ν_D and τ are also reported for each isotope, for each fit.

Table A.1: Binding energies of ^{84}Sr on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ potential.

ν	E_{obs} [GHz]	σ_E [GHz]	Fit to Eq. 3.2		Fit to Eq. 3.4	
			$E_1(\nu)$ [GHz]	δ_1 [GHz]	$E_2(\nu)$ [GHz]	δ_2 [GHz]
76	7.312	0.028	7.278	0.034	7.260	0.052
77	7.917	0.030	7.879	0.039	7.859	0.059
	7.908	0.025	7.941	-0.033	7.921	-0.013
78	8.523	0.026	8.520	0.003	8.498	0.025
79	9.210	0.028	9.205	0.004	9.181	0.029
80	9.893	0.026	9.935	-0.042	9.908	-0.015
	9.923	0.026	10.011	-0.088	9.984	-0.060
81	10.673	0.025	10.713	-0.040	10.683	-0.011
82	11.521	0.030	11.540	-0.019	11.509	0.012
83	12.417	0.028	12.421	-0.003	12.386	0.031
86	15.397	0.028	15.404	-0.007	15.362	0.035
87	16.530	0.025	16.522	0.008	16.477	0.053
89	18.878	0.028	18.962	-0.084	18.912	-0.034
91	21.681	0.026	21.695	-0.014	21.640	0.041
93	24.730	0.026	24.749	-0.019	24.689	0.041
94	26.379	0.030	26.405	-0.026	26.343	0.036
	26.409	0.028	26.575	-0.167	26.513	-0.104
95	28.099	0.028	28.152	-0.053	28.088	0.011
99	36.152	0.026	36.138	0.014	36.065	0.087
	36.107	0.028	36.359	-0.253	36.286	-0.179
100	38.361	0.024	38.405	-0.043	38.330	0.031
	38.394	0.025	38.638	-0.243	38.563	-0.168
130	187.827	0.026	187.646	0.181	187.675	0.153
131	196.713	0.027	196.536	0.177	196.578	0.135
132	205.968	0.027	205.774	0.194	205.831	0.137
	205.983	0.037	206.717	-0.735	206.776	-0.793
133	215.732	0.070	215.371	0.361	215.443	0.288
ν_D			0.874 ± 0.035		1.067 ± 0.070	
τ [ns]			5.201 ± 0.004		5.224 ± 0.008	
K [GHz]					0.029 ± 0.038	
RMSE [GHz]			0.188		0.180	

Table A.2: Binding energies of ^{86}Sr on the $5s^2\ ^1S_0 + 5s5p\ ^1P_1$ potential.

ν	E_{obs} [GHz]	σ_E [GHz]	Fit to Eq. 3.2		Fit to Eq. 3.4	
			$E_1(\nu)$ [GHz]	δ_1 [GHz]	$E_2(\nu)$ [GHz]	δ_2 [GHz]
77	7.828	0.024	7.749	0.078	7.827	0.001
78	8.457	0.022	8.374	0.083	8.449	0.008
82	11.305	0.027	11.313	-0.008	11.375	-0.070
83	12.210	0.023	12.168	0.042	12.227	-0.017
88	17.352	0.023	17.298	0.054	17.340	0.012
89	18.545	0.022	18.514	0.031	18.552	-0.007
94	25.725	0.023	25.717	0.008	25.736	-0.011
95	27.422	0.023	27.406	0.016	27.422	0.000
100	37.318	0.028	37.305	0.013	37.302	0.016
105	50.041	0.027	50.018	0.023	49.998	0.043
109	62.584	0.026	62.622	-0.037	62.590	-0.006
113	77.736	0.024	77.767	-0.031	77.726	0.009
118	100.831	0.033	100.878	-0.047	100.833	-0.002
122	123.262	0.025	123.254	0.008	123.212	0.049
127	156.958	0.030	156.899	0.059	156.874	0.085
128	164.456	0.024	164.471	-0.015	164.450	0.006
131	189.009	0.028	189.036	-0.027	189.034	-0.026
134	216.541	0.025	216.585	-0.043	216.611	-0.069
136	236.795	0.029	236.748	0.047	236.796	-0.001
ν_D			0.187 ± 0.036		0.398 ± 0.071	
τ [ns]			5.201 ± 0.004		5.224 ± 0.008	
K [GHz]					0.136 ± 0.045	
RMSE [GHz]			0.042		0.035	

Table A.3: Binding energies of ^{87}Sr on the $5s^2\ ^1\text{S}_0 + 5s5p\ ^1\text{P}_1$ potential.

ν	E_{obs} [GHz]	σ_E [GHz]	Fit to Eq. 3.2		Fit to Eq. 3.4	
			$E_1(\nu)$ [GHz]	δ_1 [GHz]	$E_2(\nu)$ [GHz]	δ_2 [GHz]
76	6.667	0.113	6.564	0.104	6.622	0.045
77	7.227	0.031	7.106	0.122	7.161	0.066
78	7.793	0.032	7.684	0.109	7.736	0.057
79	8.370	0.029	8.301	0.069	8.350	0.020
	8.374	0.035	8.365	0.009	8.414	-0.040
80	9.001	0.029	8.960	0.042	9.005	-0.004
	9.106	0.026	9.028	0.078	9.073	0.033
81	9.692	0.027	9.661	0.032	9.703	-0.010
82	10.412	0.150	10.407	0.005	10.445	-0.034
	10.454	0.027	10.484	-0.030	10.522	-0.068
83	11.256	0.028	11.200	0.056	11.235	0.021
84	12.073	0.038	12.044	0.029	12.075	-0.002
	12.108	0.031	12.131	-0.022	12.162	-0.053
85	12.993	0.028	12.939	0.054	12.967	0.027
86	13.945	0.048	13.890	0.056	13.913	0.032
87	14.950	0.033	14.897	0.053	14.917	0.033
88	15.982	0.035	15.966	0.017	15.981	0.001
	16.061	0.028	16.076	-0.014	16.091	-0.030
93	22.322	0.029	22.313	0.010	22.307	0.015
95	25.355	0.030	25.380	-0.025	25.366	-0.011
99	32.565	0.046	32.578	-0.012	32.545	0.020
100	34.552	0.041	34.620	-0.068	34.584	-0.032
105	46.428	0.036	46.508	-0.080	46.449	-0.021
108	55.053	0.035	55.148	-0.095	55.076	-0.023
109	58.204	0.030	58.309	-0.105	58.233	-0.029
110	61.488	0.057	61.619	-0.131	61.539	-0.051
142	288.180	0.026	288.176	0.004	288.170	0.010
143	300.670	0.030	300.645	0.025	300.653	0.017
144	313.570	0.034	313.560	0.010	313.584	-0.014
ν_D			0.850 ± 0.039		1.070 ± 0.075	
τ [ns]			5.201 ± 0.004		5.224 ± 0.008	
K [GHz]					0.115 ± 0.041	
RMSE [GHz]			0.063		0.033	

Table A.4: Binding energies of ^{88}Sr on the $5s^2\ ^1\text{S}_0 + 5s5p\ ^1\text{P}_1$ potential.

ν	E_{obs} [GHz]	σ_E [GHz]	Fit to Eq. 3.2		Fit to Eq. 3.4	
			$E_1(\nu)$ [GHz]	δ_1 [GHz]	$E_2(\nu)$ [GHz]	δ_2 [GHz]
65	2.581	0.004	2.537	0.044	2.580	0.001
66	2.823	0.006	2.783	0.040	2.824	-0.001
67	3.076	0.004	3.047	0.029	3.087	-0.011
68	3.371	0.004	3.333	0.038	3.371	0.001
69	3.682	0.004	3.640	0.042	3.676	0.006
71	4.357	0.006	4.326	0.031	4.359	-0.001
89	16.944	0.004	16.927	0.016	16.916	0.028
90	18.083	0.005	18.108	-0.025	18.094	-0.011
92	20.633	0.004	20.675	-0.041	20.656	-0.022
ν_D			0.493 ± 0.026		0.693 ± 0.051	
τ [ns]			5.201 ± 0.004		5.224 ± 0.008	
K [GHz]					0.067 ± 0.010	
RMSE [GHz]			0.035		0.013	

B Copy of *Photoassociative Spectroscopy of ^{87}Sr*

PHYSICAL REVIEW A **103**, 023111 (2021)

Photoassociative spectroscopy of ^{87}Sr

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We demonstrate photoassociation (PA) of ultracold fermionic ^{87}Sr atoms. The binding energies of a series of molecular states on the $^1\Sigma_u^+ 5s^2 1S_0 + 5s5p 1P_1$ molecular potential are fit with the semiclassical LeRoy-Bernstein model, and PA resonance strengths are compared to predictions based on the known $1S_0 + 1S_0$ ground-state potential. Similar measurements and analysis were performed for the bosonic isotopes ^{84}Sr and ^{86}Sr , allowing a combined analysis of the long-range portion of the excited-state potential and determination of the $5s5p 1P_1$ atomic state lifetime of 5.20 ± 0.02 ns. The results enable prediction of PA rates across a wide range of experimental conditions.

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I. INTRODUCTION

Ultracold gases of the various isotopes of strontium are currently studied for a wide range of applications, such as frequency metrology [1–3], quantum simulation of many-body physics [4,5], quantum information [6,7], Rydberg physics [8,9], and cold collisions [10–13]. The fermionic isotope (^{87}Sr) in particular attracts significant attention because it is used in optical atomic clocks [1,14] and the ground-state tenfold degeneracy arising from the large nuclear spin ($I = 9/2$) introduces novel magnetic phenomena [4]. For many of these experiments, ultracold samples are trapped in optical lattices in order to prevent atom-atom interactions or introduce spatial periodicity for quantum simulation of materials. Photoassociative (PA) spectroscopy [15,16], which is the optical formation of bound molecules from the initial state of two colliding atoms, is a well-established and useful technique for probing ultracold gases in optical lattices. It can be used to detect double occupancy of lattice sites [17], which provides a measurement of sample temperature and probe of quantum phase transitions [18]. This technique has not been utilized for ^{87}Sr , however, and no study on PA in this isotope has been published. PA formation of molecules bound in the $5s^2 1S_0 + 5s5p 3P_1$ molecular potential in ^{87}Sr was mentioned in Ref. [19], and this is more challenging than in bosonic isotopes [20–22] because of the large nuclear spin and hyperfine splitting of the molecular states.

Here, we report photoassociation in ^{87}Sr to states on the $^1\Sigma_u^+ 5s^2 1S_0 + 5s5p 1P_1$ molecular potential, to the red of the principal transition at $\lambda = 460.85$ nm. Hyperfine splitting in the excited state is small (≈ 60 MHz) and unresolved, producing a simple spectrum. We report line strengths in terms of PA collision-event rate constants for transitions across a wide range of binding energies and provide parameters for a fit of the binding energies to the semiclassical LeRoy-Bernstein

formula [23]. This can inform design of experiments using PA spectroscopy as a probe of ^{87}Sr in optical lattices. We also report LeRoy-Bernstein parameters describing molecular binding energies for ^{84}Sr and ^{86}Sr . The extracted value of the C_3 coefficient and associated $1P_1$ atomic lifetime are compared with previous results from PA spectroscopy of ^{88}Sr [24,25] and ^{86}Sr [26] and measurements of AC Stark shifts [7]. PA collision-event rate constants are compared to predictions [27] based on the known $^1\Sigma_g^+ 5s^2 1S_0 + 5s^2 1S_0$ potential [10,28].

II. EXPERIMENTAL METHODS

Using methods described in Ref. [29], ultracold strontium atoms are trapped in an optical dipole trap (1064-nm wavelength) consisting of two crossed elliptical beams propagating perpendicular to gravity with tight axis along gravity. Atoms are initially loaded into the trap and then a short stage of evaporation produces the sample used for PA spectroscopy. For ^{87}Sr , spectroscopy is performed in a trap with oscillation frequencies $(f_x, f_y, f_z) = (68, 85, 433)$ Hz. At the start of PA laser exposure, the number of atoms is $N = 2.3 \times 10^6$, the temperature is $T = 1.8 \mu\text{K}$, and the peak density is $n_0 = 2.1 \times 10^{13} \text{ cm}^{-3}$. The sample has approximately equal population of the 10 nuclear spin states [30]. For ^{84}Sr , these parameters are $(f_x, f_y, f_z) = (81, 30, 406)$ Hz, $N = 4.5 \times 10^6$, $T = 1.9 \mu\text{K}$, and $n_0 = 1.7 \times 10^{13} \text{ cm}^{-3}$. For ^{86}Sr , these parameters are $(f_x, f_y, f_z) = (61, 76, 388)$ Hz, $N = 1.2 \times 10^6$, $T = 1.8 \mu\text{K}$, and $n_0 = 1.1 \times 10^{13} \text{ cm}^{-3}$. The PA laser intensity ($3.6\text{--}237 \text{ mW/cm}^2$) and exposure time (10–1000 ms) are varied depending upon the sample and strength of the PA transition. Typical peak atom loss due to PA is 10–50%. The sample temperature varies by no more than 25% for measurements of the PA rate constant. The PA laser beam has e^{-2} radii of $w_{\text{horiz}} = 850 \mu\text{m}$ and $w_{\text{vert}} = 440 \mu\text{m}$ on the atoms, and it is treated as homogeneous over the sample.

After exposure, the PA laser and the dipole trap are extinguished, and the atom number and sample temperature are measured with resonant time-of-flight absorption imaging on

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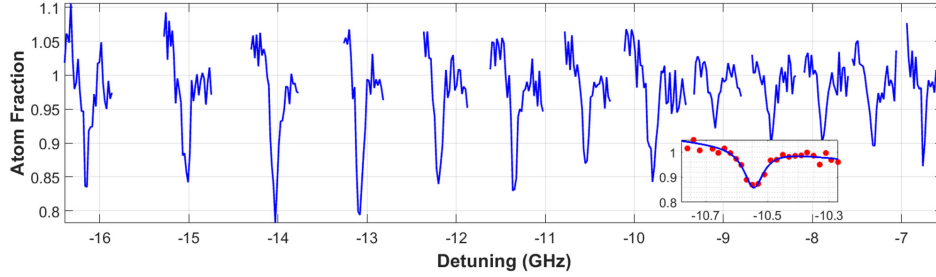


FIG. 1. Representative atom-loss spectra for excitation to molecular states on the $^1\Sigma_u^+ 5s^2 ^1S_0 + 5s5p ^1P_1$ molecular potential in ^{87}Sr . Background atom number is normalized to one. PA laser exposure times and intensities are adjusted to give comparable atom loss for all spectra, so line intensity does not reflect the PA collision-event rate constant. Exposure times and intensities vary from 75 to 200 ms and from 3.6 to 11.5 mW/cm² respectively. Inset is a representative fit to a Lorentzian.

the 461-nm transition. Photoassociation is indicated by atom loss. Figure 1 shows representative atom-loss spectra for ^{87}Sr . The PA laser is locked to a wavemeter (Moglabs FZW600) that is calibrated against the atomic $5s^2 ^1S_0 \rightarrow 5s5p ^1P_1$ transition, with a frequency accuracy of $\approx \pm 30$ MHz.

III. BINDING ENERGIES AND EXCITED-STATE MOLECULAR POTENTIAL

The PA resonances, labeled by vibrational index ν , are fit to a Lorentzian line shape. Typical linewidths range between 60 and 150 MHz. This is consistent with the lower limit given by twice the atomic linewidth $\gamma_{\text{atomic}} = 30.24$ MHz [25]. The dominant source of additional line broadening is laser frequency jitter. Binding energies (defined as $E_\nu > 0$) are determined by taking the difference between PA resonance positions and the wave number corresponding to excitation of the $5s^2 ^1S_0 \rightarrow 5s5p ^1P_1$ atomic resonance.

The long-range form of the excited-state $^1\Sigma_u^+ ^1S_0 + ^1P_1$ molecular potential can be approximated as

$$V_e(r) = D - \frac{C_3}{r^3} + \frac{\hbar^2[J(J+1)+2]}{2\mu r^2}, \quad C_3 = \frac{3\hbar\lambda^3}{16\pi^3\tau}, \quad (1)$$

where D is the dissociation energy, μ is the reduced mass, r is the internuclear separation, and $\tau = 1/(2\pi\gamma_{\text{atomic}})$ is the lifetime of the 1P_1 atomic state. Because of the ultracold temperature, only s -wave collisions occur and only $J = 1$ molecular rotational states are excited. The rotational energy is small and can be neglected, as can thermal energy of the initial collisional state. The binding energies, E_ν , can be fitted to the semiclassical Leroy-Bernstein formula [23]:

$$E_\nu = [(\nu - \nu_D)H_3]^6, \quad H_3 = \frac{1}{C_3^{1/3}} \frac{\hbar\Gamma(\frac{4}{3})}{2\Gamma(\frac{5}{6})} \sqrt{\frac{2\pi}{\mu}}, \quad (2)$$

where $\nu = 1$ corresponds to the least-bound state, Γ is the gamma function, and ν_D is a fit parameter ranging from 0 to 1 that takes on a different value for each isotope. We perform a combined fit of all data to Eq. (2) using a common value of C_3 as a fit parameter and independent values of ν_D for each isotope. The quantum numbers ν assigned to each level are shifted to obtain $0 < \nu_D < 1$.

Figure 2 shows binding energies for ^{87}Sr and residuals for all isotopes. Table I shows the fit parameters, including the value of τ extracted from the C_3 coefficient. The statistical uncertainty in τ from this procedure is very small, but the fit residuals for all three isotopes show a systematic trend corresponding to ≈ 100 MHz variation over a change

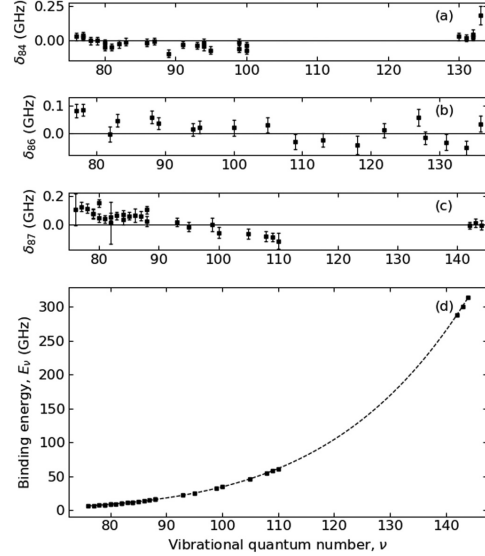


FIG. 2. Fit of the binding energies of states on the $^1\Sigma_u^+ 5s^2 ^1S_0 + 5s5p ^1P_1$ molecular potential for various strontium isotopes. Plots (a)–(c) show the difference (δ) between observed and fit values for the binding energies for ^{84}Sr , ^{86}Sr , and ^{87}Sr respectively, using parameters from Table I. Plot (d) shows the measured binding energies as a function of vibrational quantum number, ν , for ^{87}Sr . The dashed line is the best fit of the data to Eq. (2).

TABLE I. Parameters from a fit of binding energy for ^{84}Sr , ^{86}Sr , and ^{87}Sr to Eq. (2).

Isotope	^{87}Sr	^{86}Sr	^{84}Sr
ν_D	0.87 ± 0.02	0.20 ± 0.02	0.87 ± 0.02
τ (ns)		5.20 ± 0.02	

of ≈ 100 GHz in binding energy. This trend might indicate systematic wavemeter error, variation in molecular-state AC Stark shifts from the optical dipole trap laser fields, or the influence of additional terms in the molecular potential not accounted for by the Leroy-Bernstein formula [31]. Adding an additional fit parameter in the form of a binding energy offset removes the systematic trends in the residuals and increases τ by 0.02 ns or 0.4%, which we take as our uncertainty. We thus quote a final value of $\tau = 5.20 \pm 0.02$ ns. The value of τ determined here differs by 1% from the most accurate reported measurement of $\tau = 5.263 \pm 0.004$ ns, performed with photoassociation in an optical lattice [25], and is in closer agreement with a more recent value of $\tau = 5.234 \pm 0.008$ ns determined from AC Stark shifts of Sr levels [7]. The binding energies for all observed transitions are included in the Supplemental Material [32].

IV. PHOTOASSOCIATIVE LOSS

The loss of atoms due to photoassociation is described by a local equation for the evolution of the atomic density

$$\dot{n} = -\beta(I, f)n^2 - \Gamma_1 n, \quad (3)$$

where Γ_1 describes one-body loss due to light scattering on the atomic transition or background gas collisions, and the two-body loss is described by β , which depends on PA laser intensity, I , and frequency, f . Assuming constant sample temperature, the number of atoms in the trap as a function of the PA exposure time t is given by

$$N(t) = \frac{N_0 e^{-\Gamma_1 t}}{1 + \frac{n_0 \beta}{2\sqrt{2}\Gamma_1} (1 - e^{-\Gamma_1 t})}, \quad (4)$$

where N_0 is the number at the beginning of the PA interaction time and n_0 is the initial density. The density can be calculated from the number and sample temperature, approximating the trap as an infinitely deep harmonic potential with oscillation frequencies matching the measured frequencies of the optical trap. Equation (3) has been integrated over volume to yield the evolution of sample number, which is solved by Eq. (4).

Near resonance with the transition to a molecular state with vibration quantum number ν and center frequency f_ν , the PA loss is described with a Lorentzian line shape [26],

$$\beta = \frac{2K_\nu \gamma_{\text{mol}}}{\gamma} \frac{1}{1 + 4(f - f_\nu)^2 / \gamma^2}, \quad (5)$$

where $\gamma_{\text{mol}} = 2\gamma_{\text{atomic}}$ is the natural linewidth of the PA transition due to radiative decay of the molecular state and γ is the observed linewidth of the transition. K_ν , which is proportional to laser intensity I , is the resonant collision-event rate constant that would be observed in the absence of any broadening beyond the natural linewidth. Thermal broadening is much

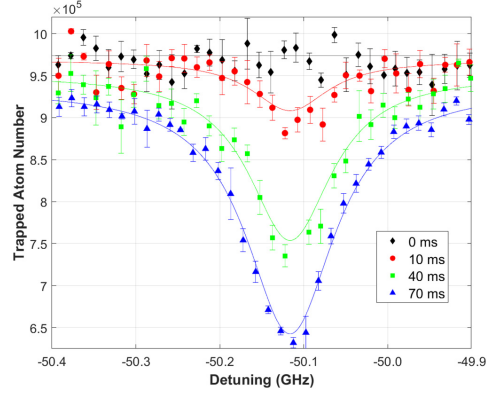


FIG. 3. Atom-loss spectra for PA to the $\nu = 105$ state of the $^1\Sigma_u^+ 5s^2 1S_0 + 5s5p 1P_1$ molecular potential for ^{86}Sr . PA laser exposure time is indicated in the legend. A combined fit of all data to Eqs. (4) and (5) determines the the peak PA collision-event rate constant K_ν . The PA laser intensity is 3.6 mW/cm^2 and the initial density is $n_0 = 1.3 \times 10^{13} \text{ cm}^{-3}$. The fit result is $K_\nu/I = 2.8 \times 10^{13} \text{ cm}^3/(\text{s mW})$.

smaller than γ_{mol} and the laser intensity is low enough that saturation effects are negligible.

Figure 3 shows a fit of typical atom-loss spectra to Eqs. (4) and (5) for different PA laser exposure times for ^{86}Sr . All fit parameters are well determined, but systematic uncertainty in laser intensity, atom density, and sample temperature lead to systematic uncertainty of about a factor of 3 in the fundamental quantity for comparison with theory, K_ν/I .

K_ν/I is proportional to $F_{\text{eg}}^\nu(E, \Delta_\nu)$, the free-bound Franck-Condon factor for excitation to the excited state ν from the ground $^1\Sigma_g^+ 5s^2 1S_0 + 5s^2 1S_0$ potential, where E is the initial collision energy and $\Delta_\nu < 0$ is the detuning from atomic resonance. Through the relation

$$h\Delta_\nu = V_e(r_C^\nu) - D - V_g(r_C^\nu), \quad (6)$$

the detuning defines the Condon radius, r_C^ν , which is the internuclear separation at which the photon energy (via the Planck constant h), is resonant with the difference in molecular potentials. r_C^ν can be interpreted as the classical separation at which excitation occurs. At long range and ultracold temperatures, the ground potential can be approximated by $V_g(r) = -C_6/r^6 - C_8/r^8 - C_{10}/r^{10}$.

Using the reflection approximation [27], the Franck-Condon factor can be related to the energy-normalized ground-state wave function at the Condon point, $\Psi_g(r_C^\nu, E)$ through

$$F_{\text{eg}}^\nu(E, \Delta_\nu) = \frac{\partial E_\nu}{\partial \nu} \frac{1}{d_\nu} |\Psi_g(r_C^\nu, E)|^2 \quad (7)$$

where $\partial E_\nu / \partial \nu$ is the spacing between adjacent vibrational levels in the excited state at level ν , which can be found from

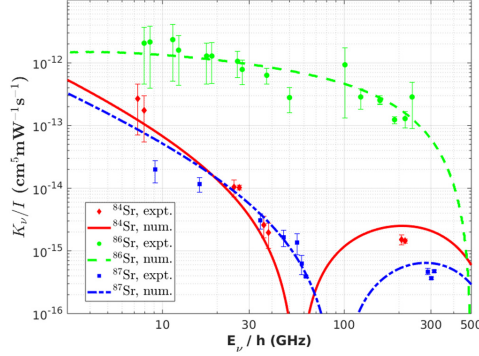


FIG. 4. Intensity-normalized resonant collision-event constant (K_v) for strontium PA transitions. Solid lines are predictions based on Franck-Condon factors derived from numerically calculated ground-state wave functions [Eq. (7)] as described in the text.

Eq. (2). Also,

$$d_c = \left. \frac{d}{dr} [V_e(r) - V_g(r)] \right|_{r=r_c} \quad (8)$$

is the difference in slopes of the excited and ground potentials.

V. RATE-CONSTANT MEASUREMENTS

We calculate ground-state wave functions for a collision energy of $2 \mu\text{K}$ by numerically integrating the Schrödinger equation [33]. We use the full ground-state potential from Ref. [28] in the form from Ref. [34] with recommended values of $C_6 = 1.525 \times 10^7 \text{ cm}^{-1} \text{ \AA}^6$, $C_8 = 5.159 \times 10^8 \text{ cm}^{-1} \text{ \AA}^8$, and $C_{10} = 1.91 \times 10^{10} \text{ cm}^{-1} \text{ \AA}^{10}$. Figure 4 shows the measured values of K_v/I and theoretically expected values based on the calculated wave functions. A common scaling factor is applied to theoretical predictions to account for the proportionality between K_v/I and the Franck-Condon factors. Predicted rates for ^{87}Sr are further reduced with respect to the bosons by the ratio of the pair correlation functions $g_f^{(2)}/g_b^{(2)}$, where $g_b^{(2)} = 2$ reflects bunching for bosons and $g_f^{(2)} = 0.9$ reflects Pauli exclusion for a gas of identical fermions in ten equally populated internal states [30]. Measurements for ^{86}Sr agree within a factor of 2 with previously reported values [26], which is reasonable given systematic uncertainties.

The rate coefficients go to zero when the Condon radius for the transition is near a node of the ground-state wave function (Fig. 4). For ^{87}Sr and ^{84}Sr , the node interrogated by measurements reported here corresponds to internuclear spacing equal to the s -wave scattering lengths, $a_{84} = 123 a_0$ or

$a_{87} = 96 a_0$ [10], where a_0 is the Bohr radius. For ^{86}Sr , $a_{86} = 823 a_0$ is a larger length scale than probed here, and the node corresponding to $\Delta = -500 \text{ GHz}$ is the second preasymptotic node [26].

VI. PHOTOASSOCIATION IN AN OPTICAL LATTICE

For ^{87}Sr and ^{84}Sr , the two isotopes most often used for quantum-gas research [1,2,4,5,9], the PA rate constants are relatively small at convenient detunings for experiments. A useful figure of merit is the ratio of the number-loss rate for PA of two atoms in a single lattice site ($\dot{N}_{\text{PA}}$) to the off-resonant, single-atom, photon-scattering rate ($R \approx 2\pi s_0 \gamma_{\text{atomic}}^3 / \Delta^2$). The ratio of laser intensity to the atomic transition's saturation intensity ($I_{\text{sat}} = 40 \text{ mW/cm}^2$) is indicated by s_0 .

For two ^{87}Sr atoms in a single site of an optical lattice, each of mass m , $\dot{N}_{\text{PA}} \approx 2K_v \int d^3r n^2(r) = 2K_v / (2\pi a_{\text{HO}}^2)^{3/2}$, where we have assumed the atoms are both in the ground state of a single site in a deep optical lattice in different internal spin states [35]. $a_{\text{HO}} = \sqrt{\hbar/m\omega}$ is the harmonic oscillator length for $\omega = \sqrt{4V_0 E_R}/\hbar$ and lattice depth V_0 . $E_R = 2\pi^2 \hbar^2 / (m \lambda_{\text{lat}}^2)$ is the recoil energy for lattice laser wavelength λ_{lat} . For $\lambda_{\text{lat}} = 1064 \text{ nm}$ and $V_0 = 16E_R$, $1/(2\pi a_{\text{HO}}^2)^{3/2} = 1 \times 10^{14} \text{ cm}^{-3}$. For PA at small detuning ($\Delta = -10 \text{ GHz}$), $\dot{N}_{\text{PA}} \approx 3 \times R$. For detuning beyond the wave-function node ($\Delta = -300 \text{ GHz}$), $\dot{N}_{\text{PA}} \approx 13 \times R$, which is more favorable. At $\Delta = -300 \text{ GHz}$, a PA laser intensity of $20I_{\text{sat}}$ yields $\dot{N}_{\text{PA}} \approx 10/\text{s}$.

VII. CONCLUSION

In summary, we have measured and characterized photoassociation resonances up to $\approx 314 \text{ GHz}$ red detuned from the atomic asymptote of the $^1\Sigma_u^+ 5s^2 1S_0 + 5s5p 1P_1$ molecular potential in fermionic ^{87}Sr . Similar measurements were made in bosonic ^{86}Sr and ^{84}Sr , and a combined fit to the semiclassical LeRoy-Bernstein model allowed determination of the $1P_1$ atomic state lifetime and other spectroscopic parameters. Resonance intensities were compared with predictions from a reflection approximation and the ground-state wave function calculated with the best available ground-state potential. We find that, to within experimental uncertainties, the resonance frequencies and intensities are reasonably well described by theoretical predictions. This work will enable accurate prediction of photoassociative transition frequencies and rates for experiments with the strontium isotopes most commonly used in quantum gas experiments, including experiments with fermionic ^{87}Sr .

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