Precision optical metrology with alkali-atom isoclinic points

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Abstract. Vapour-phase spectroscopy rarely involves transitions between well-isolated atomic states. Routinely, the spectra comprise overlapped Doppler/pressure-broadened resonances, which leads to a “pulling” of the spectral peaks from their true atomic resonance frequencies. This pulling gives the absorption resonances a temperature sensitivity, which limits their utility for precision spectroscopy when sub-Doppler techniques are not viable. Here, we discuss the use of alkali isoclinic points as a solution to this problem.

1. Introduction

Though vapor-phase spectroscopy is ubiquitous in atomic physics, it rarely involves the text-book case of well-isolated quantum state transitions. More often, the spectra comprise overlapped Doppler/pressure-broadened resonances, with the overlap yielding spectral peaks that are “pulled” from their true atomic resonance frequencies. Further, as vapor temperature fluctuates the Doppler-broadened widths vary, which in turn leads to more or less spectral overlap, and as a consequence fluctuations in resonance pulling. Thus, the resonance peaks in a vapor phase spectrum rarely provide an accurate measure of the atom’s intrinsic resonance frequency, and they are routinely sensitive to systematic temperature variations. Though sub-Doppler spectroscopy has long been recognized as a means for mitigating such problems, it is not viable under all conditions: sub-Doppler signals can be sensitive to microphonics, and sub-Doppler techniques are inoperative in regimes of collision broadening. Here, we discuss the use of alkali isoclinic points for high-precision and high-accuracy vapor-phase spectroscopy when sub-Doppler techniques fail.

According to the IUPAC Compendium of Chemical Terminology, an isoclinic point is “a wavelength, wavenumber, or frequency at which the first derivative of an absorption spectrum of a sample does not change upon a chemical reaction or physical change of the sample” [1]. If we take this to include changes in state variables (e.g., temperature and pressure), then the $D_1$ spectra of $I = 3/2$ alkalis contain isoclinic points (where $I$ is the nuclear spin) [2], and these correspond to the midpoint between their $n^2S_{1/2}(F_g=2) \rightarrow m^2P_{1/2}(F_e=1,2)$ transitions as illustrated in figure 1. Specifically, given the equality of the absorption cross sections for the $|F_g=2\rangle \rightarrow |F_e=1,2\rangle$ transitions (i.e., the “doublet”), the amplitudes of these two over-lapped absorption resonances are identical. Consequently, any state-variable that only influences the widths of the lines (e.g., temperature via Doppler broadening or alkali pressure via collision broadening) will not affect the midpoint’s frequency, $\nu_m$: the zero-crossing of the absorption’s first derivative at $\nu_m$ will not change with temperature or pressure. Alkali isoclinic points

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can therefore be employed as state-variable independent atomic frequency references, either for laser stabilization, or as “markers” against which other (state-variable dependent) spectral features can be measured [3,4]. In the following sections we discuss some of these applications.

2. Present experimental system

2.1. Measurement system

Figure 2 shows our typical experimental arrangement: a VCSEL diode laser is split into two beams, each of which has a diameter of 0.4 cm, and is separately attenuated using a rotating polarizer. One beam passes through the reference cell, which contains a vapor of isotopically enriched $^{87}$Rb without any buffer gas, maintained at $35 \pm 0.01$ °C. The other beam passes through the measurement cell, whose temperature $T$ can be varied between 32.5 °C and 60 °C, and which routinely contains $^{87}$Rb in the presence of a buffer gas. The cell diameters are 2.5 cm and their lengths are 4.4 cm, and we employ low laser powers to limit distortions of the spectra due to optical pumping (on the order of $10^2$ nW).

The relative absorption cross section in both cells, $\sigma(\nu)$, is estimated using Beer’s law: $\Sigma(\nu)L = \ln[I(\nu)/I_0(\nu)]$, where $I(\nu)$ is the transmitted light intensity and $I_0(\nu)$ is the light intensity reaching the photodetector in the absence of the vapor, each evaluated at laser frequency $\nu$. $I_0(\nu)$ can be estimated by tuning the laser both above and below resonance, and fitting the off-resonance transmitted light intensity to a quadratic in $\nu$.

2.2. Measuring resonance shifts

The midpoint point frequency in each cell (i.e., $\nu_m$ in figure 1) is determined by taking a numerical derivative of the absorption cross section, with the isoclinic point in the reference cell providing a temperature independent frequency marker for the spectral features observed in the measurement cell. The frequency separation between the two cells’ midpoint frequencies is a measure of the $D_1$ frequency shift for the Rb atoms in the measurement cell due to temperature and/or buffer gas pressure. Figure 3a shows the relative absorption cross sections in our reference and measurement cells for the case of 25 torr Kr in the measurement cell at a temperature of 42.5 °C. Figure 3b shows the numerical derivatives of the absorption cross sections, and highlights the $^{87}$Rb atom’s $D_1$ collision shift in this system. (Though
the spectra look “clean” in figure 3a, taking the numerical derivative of the data makes the noise in the spectra manifest.)

Figure 2: Experimental arrangement for our present isoclinic-point spectroscopy experiments.

Figure 3: (a) The relative absorption cross section in our reference cell and our measurement cell at 42.5 °C with 25 torr Kr. (b) The numerical derivative of the absorption cross sections, indicating the collision shift of the $^{87}$Rb $D_1$ line in the measurement cell. Abscissa values in “scan time” are calibrated to frequency using the known excited-state hyperfine splitting of $^{87}$Rb (as observed in the reference cell) after taking account of Doppler broadening’s pulling of the lineshape peaks.
3. Some recent isoclinic point applications

3.1. Accurate measurement of collision shifts

With the isoclinic point, we can make very accurate measurements of collision shifts. Recently, we compared the Rb/Kr and Rb/Xe D$_1$ collision shifts with theory [5], and as illustrated in figure 4 the experimental uncertainty in the collision shifts for these systems has been steadily decreasing over time. In particular, the most recent measurements by Rotondaro and Perram [6] and our group are in excellent agreement. In this regard, it is important to note that the results from our two groups were obtained by very distinct measurement techniques: Rotondaro and Perram employed a traditional spectroscopic technique to estimate the center-of-mass collision shift of the hyperfine absorption manifold, whereas we employ the $^{87}$Rb isoclinic point. Thus, while unknown systematic effects might unduly influence our results or equivalently those Rotondaro & Perram, it is difficult to imagine a systematic effect that would influence both techniques in the same way and to the same extent.

The figure also shows that there is a slight, but statistically significant discrepancy between theory and experiment (i.e., ~ 20%). The theories of both Rebane [7] and Kielkopf [8] overestimate the collision shifts. While Kielkopf’s modeling of the interaction potential is more detailed than Rebane’s (as Kielkopf considers a quadrupole, 1/R$^3$, term in the potential [9]), Rebane’s theory explicitly accounts for the fine and hyperfine structure of the alkali. Interestingly, both theories determine the magnitude of the van der Waals ground and excited-state coefficients of the interaction potential in a similar fashion, suggesting that there is a need for a closer theoretical examination of the noble-gas atom’s interaction with the alkali $^2$P$_{1/2}$ state. (The alkali ground-state’s interaction with the noble gases is arguably better understood than the excited-state interaction, suggesting the later as the more likely suspect for error.)

3.2. The collision shift’s energy dependence

The energy dependence of the collision cross section gives rise to a temperature dependence of the D$_1$ collision shift: $\delta\nu(T) = \delta\nu(T_0) \times (T/T_0)^\kappa$, where $\delta\nu(T)$ is the collision shift at temperature $T$, and $T_0$ is a reference temperature. Though the temperature exponent, $\kappa$, provides unique information regarding the perturbative interaction [14], measurements of $\kappa$ have proven difficult. In large part, this stems from attempting to measure small changes in the center-of-mass shift of a manifold of optical hyperfine transitions as the manifold shifts and broadens with temperature (e.g., figure 1). One of the few unambiguous techniques relies on the isoclinic point [3].

Figure 5 shows a complete set of published experimental $\kappa$ exponents for the Rb and Cs D$_1$ transitions: A $\Rightarrow$ Romalis et al. [13], B $\Rightarrow$ Kluttz et al. [15], C $\Rightarrow$ Kozlova et al. [16], D $\Rightarrow$ Wells et al. [3], E $\Rightarrow$ Wells et al. [5]; circles correspond to Rb, while diamonds correspond to Cs. The dashed
(brown) and long-dash (blue) lines correspond to the only theoretical estimates of $\kappa$ for Rb and Cs, respectively [8]. Barring the isoclinic point measurements, the general scatter of the experimental data among themselves, and between experiment and theory, is much larger than the quoted experimental uncertainties. This attests to the difficulty of $\kappa$ exponent measurements using traditional spectroscopic techniques. Conversely, the Rb/Kr and Rb/Xe $\kappa$ exponents based on isoclinic point measurements are not only consistent with one another (as one would expect for Rb interacting with the heavier noble gases), but agree very well with theory: $\kappa_{\text{th}} = 0.31$ [8].

![Figure 5: Complete set of published $\kappa$ exponent values for the Rb and Cs D$_1$ collision shifts. The dashed lines correspond to theory, which overlap beyond Ne. Barring the isoclinic point measurements, the scatter in the data attests to the difficulty of $\kappa$ measurements, even though $\kappa$ provides fairly unique information regarding the perturbative interaction.](image)

3.3. Understanding the detailed character of the isoclinic point

The isoclinic nature of the midpoint between the ‘a’ and ‘b’ transitions illustrated in figure 1 requires the equality of oscillator strengths for the $5^2S_{1/2}(F=2) \rightarrow 5^2P_{1/2}(F=1)$ and $5^2S_{1/2}(F=2) \rightarrow 5^2P_{1/2}(F=2)$ transitions. Any process that breaks that equality destroys the isoclinic nature of the midpoint, which has prompted research in our laboratory carefully examining ‘a’ and ‘b’ transition-amplitude asymmetry.

![Figure 6: We measured the asymmetry parameter $\alpha$ (defined in the text) as a function of Xe pressure (circles). (The diamond corresponds to a cell that was mostly filled with Xe, but had a small amount of additional N$_2$: total pressure, $P_T = 18.0$ torr, $P_{Xe}/P_T = 0.98$.) The measured asymmetry agrees very well with a theory ascribing the asymmetry to mixing of the $P_{1/2}$ and $P_{3/2}$ oscillator strengths.](image)

Recently, we found evidence that elastic $P_{1/2} \leftrightarrow P_{3/2}$ fine-structure mixing collisions add $D_2$ oscillator strength into the $D_1$ transition [17] causing an isoclinic point asymmetry. Our results are shown in figure 6, where the asymmetry parameter, $\alpha$, is defined as the relative change in the ‘a’ and ‘b’ transition amplitudes (i.e., $S_a$ and $S_b$, respectively):
\[
\alpha = \frac{2(S_a - S_b)}{S_a + S_b}
\]

(1)

As the figure shows, this collision process has a small but noticeable effect on the equality of the ‘a’ and ‘b’ transition amplitudes, and our measurements are in very good agreement with a theory ascribing the asymmetry to \(P_{1/2} \leftrightarrow P_{3/2}\) oscillator-strength mixing [17]. We note, however, that while the asymmetry is observable, it likely has little influence on the utility of the isoclinic point for most precision spectroscopy purposes [17].

4. Summary

Here, we have discussed the alkali isoclinic point, i.e., the midpoint between the \(n^2S_{1/2}(F=2) \rightarrow n^2P_{1/2}(F=1,2)\) transitions in (nuclear spin) \(I = 3/2\) alkalis, and some recent isoclinic-point applications. In particular, alkali isoclinic points can be employed as state-variable independent atomic frequency references, which can be employed for laser stabilization, or as “markers” against which other (state-variable dependent) spectral features can be measured. To date, isoclinic points have been employed to make precision measurements of collision shifts and the energy dependence of those shifts [3,5]. In our laboratory, we are continuing to exploit isoclinic points in order to explore rubidium’s interaction with diverse perturbers, notably collision shift and \(\kappa\) measurements for Rb interacting with He, Ne, Ar, and \(N_2\). Additionally, we are working to develop a thermometry capability based on isoclinic points, which will (potentially) lead to the improved long-term stability of vapour-cell atomic clocks [4].

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