

Rubidium D_1 collision shift by heavy noble gases

N. P. Wells, T. U. Driskell, and J. C. Camparo

Physical Sciences Laboratories, The Aerospace Corporation, PO Box 92957, Los Angeles, California 90009, USA

(Received 18 August 2015; published 13 October 2015)

Using an isoclinic-point technique, we measured the D_1 collision shift by Xe, $\partial[\delta\nu]/\partial P$, and the exponent κ of the shift's temperature dependence (i.e., $\delta\nu \sim T^\kappa$). As demonstrated in our examination of the Rb-Kr system [N. P. Wells *et al.*, *Phys. Rev. A* **89**, 052516 (2014)], the isoclinic point provides (arguably) the only means of assessing κ unambiguously: $\kappa_{\text{Kr}} = 0.36 \pm 0.06$ and in the present work $\kappa_{\text{Xe}} = 0.32 \pm 0.05$. With our estimate of κ for the Rb-Kr and Rb-Xe systems, we were able to combine our Kr and Xe collision shift measurements with those of Rotondaro and Perram [M. D. Rotondaro and G. P. Perram, *J. Quant. Spectrosc. Radiat. Transfer* **57**, 497 (1997)] (another set of high quality $\partial[\delta\nu]/\partial P$ measurements) to obtain a highly accurate experimental estimate for the D_1 collision shift resulting from Rb's interaction with the heavy noble gases: For the Rb-Kr interaction $\partial[\delta\nu]/\partial P|_{T=323\text{K}} = -5.02 \pm 0.07$ MHz/torr and for the Rb-Xe interaction $\partial[\delta\nu]/\partial P|_{T=323\text{K}} = -5.46 \pm 0.09$ MHz/torr. These measured values for the collision-shift coefficient are approximately 20% smaller (in magnitude) than the best theoretical estimates, suggesting that there is room for theoretical improvement regarding our present understanding of how noble-gas collisions perturb the alkali-metal $P_{1/2}$ state.

DOI: [10.1103/PhysRevA.92.042509](https://doi.org/10.1103/PhysRevA.92.042509)

PACS number(s): 32.70.Jz, 32.30.Jc, 34.20.Cf

I. INTRODUCTION

The perturbation of an alkali-metal atom's optical absorption lines by the heavier noble gases has been a topic of continuing interest for a number of years. In large part, this interest stems from the relative simplicity of the alkali-metal–noble-gas system: A closed-shell noble-gas atom with relatively large polarizability [1] perturbs the single valence electron of the alkali metal principally via a van der Waals $1/R^6$ interaction. Not only does this make for tractable theoretical computation [2–4], but it can clarify the interpretation of experimental line broadening and line shift measurements (e.g., there is no alkali-metal–to–perturber energy transfer, as can occur with molecular species [5,6]). Consequently, the alkali-metal–noble-gas system provides fertile ground for detailed investigations of atom–atom interactions; and though both line broadening and line shifts are routinely calculated and measured (since they carry complementary information regarding the alkali-metal–noble-gas interaction [7,8]), high-accuracy measurements of either can provide a critical test of theory.

Historically, collisional broadening has received the greatest attention. However, at low noble-gas densities, where theory is likely to be most accurate due to the dominant role played by binary collisions, the measurement of collision-broadened linewidths can be quite difficult. Specifically, in the low noble-gas pressure regime the spectroscopically observed Voigt line shapes are largely determined by Doppler broadening [9], which masks the collision broadening of primary interest. Moreover, in order to disentangle a collision-broadening coefficient from a measured Voigt linewidth, one must account for natural broadening's contribution to the line shape as well as the effect of laser phase fluctuations [10–13].

Though the Doppler effect should have minimal to no influence on collisional line shifts $\delta\nu$, the measurement of line shifts is no less problematic. Routinely, alkali-metal resonance lines correspond to a manifold of optical hyperfine transitions, which may be only partially resolved [14,15]. Consequently, in order to determine a manifold's center-of-mass shift, which is the object best suited for comparison with theory, one must

accurately account for the overlapping wings of the individual Voigt line shapes, which can be a nontrivial problem [16]. Moreover, as the temperature of a vapor changes (and the Doppler widths of the various resonances change), there is a temperature-dependent pulling of the line-shape peaks within the manifold.

In previous work we discussed the use of alkali-metal isoclinic points as very stable frequency markers for precision spectroscopy [17]. Briefly, an isoclinic point is a wavelength, wave number, 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 [18]. If we take this to include changes in state variables (e.g., temperature and pressure), then the D_1 spectra of $I = 3/2$ alkali metals contain isoclinic points (where I is the nuclear spin) and these correspond to the midpoint between their $n^2S_{1/2}(F_g = 2) - m^2P_{1/2}(F_e = 1, 2)$ transitions as illustrated in Fig. 1 for the case of ^{87}Rb . Using the ^{87}Rb isoclinic point, we were recently able to make precision measurements of the Kr D_1 collision shift $\delta\nu$ without many of the systematic effects that have plagued previous line-shift measurements [19]. In particular, we were able to determine the density dependence of the collision shift (i.e., $\partial[\delta\nu]/\partial P$, where P is the noble-gas pressure) with an accuracy of $\pm 0.6\%$, which is to be compared with the previous best measurements of $\partial[\delta\nu]/\partial P$ in this system: $\pm 2.0\%$ [20] and $\pm 1.9\%$ [21]. Moreover, the isoclinic-point technique simultaneously provided a fairly accurate determination of the line shift's temperature exponent κ [i.e., $\delta\nu(T) = \delta\nu(T_0) \times (T/T_0)^\kappa$], allowing for unambiguous comparisons to theory and other experiments carried out under diverse temperature conditions.

In the present work we extend our previous measurements to the Rb D_1 collision shift by Xe and again determine both $\partial[\delta\nu]/\partial P$ and κ . The significance of the present work, however, is not solely a more accurate cataloging of $\partial[\delta\nu]/\partial P$ and κ for the Rb-Xe system. Rather, taken together with previous measurements in the Rb-Xe system as well as the Rb-Kr system, the systematic and random experimental uncertainties are now low enough that the experimental

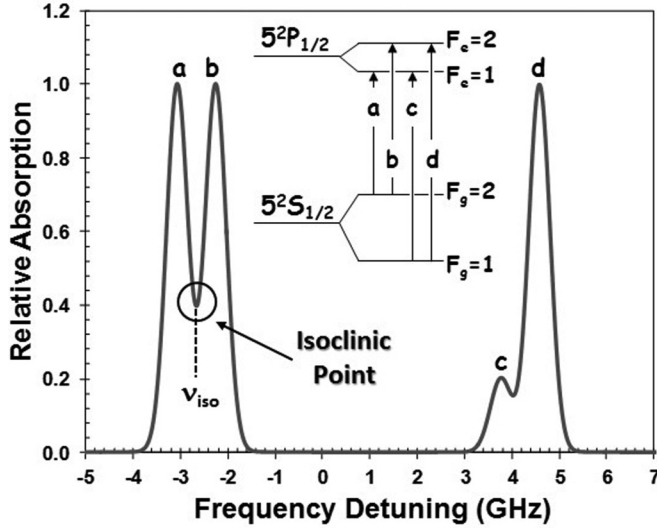


FIG. 1. ^{87}Rb D_1 absorption spectrum showing the isoclinic point corresponding to the midpoint between the $5^2S_{1/2}(F_g = 1) \rightarrow 5^2P_{1/2}(F_e = 1, 2)$ absorption resonances.

values for $\partial[\delta\nu]/\partial P$ provide a fairly stringent test of theory regarding the alkali-metal–heavy-noble-gas interaction.

In the following section we review our experimental system for isoclinic-point line-shift measurements and provide our present assessments of $\partial[\delta\nu]/\partial P|_{T_0}$ and κ (i.e., the density dependence of the collision shift at the reference temperature T_0) for the Rb-Xe system. Then, in Sec. III we consider the measured values of κ for both the Rb-Xe and Rb-Kr systems, and discuss the manner in which these values provide a direct measure of the power-law form of the alkali-metal–noble-gas difference potential (e.g., $1/R^6$), which places a constraint on theory independent of $\partial[\delta\nu]/\partial P|_{T_0}$. In Sec. IV we compare experimental and theoretical values of $\partial[\delta\nu]/\partial P$ in both the Rb-Kr and Rb-Xe systems, and demonstrate a statistically significant $\sim 20\%$ discrepancy between theory and experiment. While relatively small, such a discrepancy nonetheless suggests room for improvement in our theoretical understanding of the alkali-metal–noble-gas interaction. In particular, based on the experimental values of κ , which suggest that the difference potential is dominated by a $1/R^6$ term, the theory-experiment $\partial[\delta\nu]/\partial P$ discrepancy suggests an incomplete theoretical understanding of the van der Waals interaction strength for the alkali-metal $P_{1/2}$ state.

II. EXPERIMENT

A. Overview

Figure 2 shows our experimental arrangement: The output of a vertical-cavity surface-emitting 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 with a nominal power of about 100 nW passes through the reference cell, which contains a vapor of ^{87}Rb (no buffer gas) maintained at $35 \pm 0.01^\circ\text{C}$. The other beam with a similar power passes through the measurement cell, whose temperature T is varied between 32.5°C and 60°C and which contains a mixed ^{87}Rb -Xe vapor. Our vertical-cavity surface-emitting laser linewidth

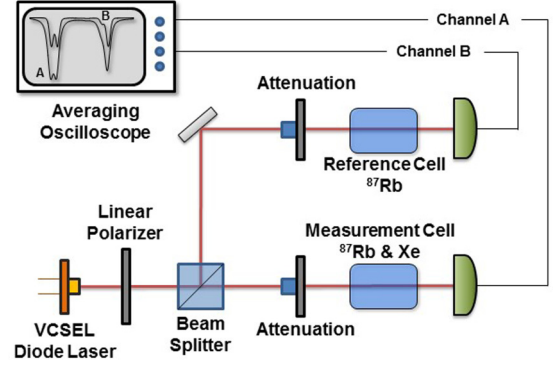


FIG. 2. (Color online) Experimental arrangement.

is 50 MHz (full width at half maximum) and the cell diameters are 2.5 cm. The measurement cells have a length L of 4.4 cm and the reference cell has a length of 2.5 cm.

We employed four different measurement cells in our experiments, each containing different Xe pressures: 3.5, 8.7, 16.9, and 26.0 torr. The Xe pressures in the closed cells were measured using the technique of Kazantsev *et al.* [22]. Briefly, the Xe cells were taken to a separate atomic-clock-system setup, and employed as the test clock's resonance cell [23]. The frequency shift of the test clock, relative to a GPS-disciplined Rb atomic clock, is dominated by the hyperfine transition's pressure shift [24], and is therefore a measure of the Xe pressure in the cell. In separate measurements we verified that this technique has an absolute accuracy better than ± 0.2 torr and a measurement repeatability of $\sim \pm 0.01$ torr [25].

B. Measurement procedure

Similar to our previous work [19], we recorded the absorption cross section in our two cells as a function of time during a laser frequency sweep over the D_1 manifold of absorption resonances. The absorption cross section $\sigma(\nu)$ was estimated using Beer's law $N\sigma(\nu)L = \ln[I(\nu)/I_0(\nu)]$, 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 at laser frequency ν ; this was estimated by tuning the laser both above and below resonance and fitting the off-resonance transmitted light intensity to a quadratic in ν . Here N is the density of ^{87}Rb atoms in the vapor. We calibrated the time difference between the a and b transitions of Fig. 1 to the excited-state hyperfine splitting (after accounting for the fact that the resonances' separation will be slightly smaller than the excited-state hyperfine splitting due to the overlap of the resonance lines). Then, taking a numerical derivative of our absorption spectra, we estimated the zero crossings of the isoclinic points in our reference and measurement cells, and the difference between these two isoclinic point frequencies was our measure of the collision shift at temperature T : $\delta\nu_{\text{iso}}(T)$ [26].

To limit distortions of the spectra due to repopulation optical pumping, which creates an amplitude asymmetry between the a and b resonances (and therefore a systematic shift of the isoclinic point), we worked at relatively low laser intensities [27]. More specifically, we measured $\delta\nu_{\text{iso}}(T)$ at a series of specific temperatures and repeated the set of measurements

for a range of laser intensities. We employed several steps in our data analysis procedure.

(i) *Restrict the range of laser intensities that will be employed for the determination of $\partial[\delta\nu]/\partial P$ and κ .* At each laser intensity, we employed a quadratic least-squares fit to estimate the pressure shift at $T_0 = 45^\circ\text{C}$: $\delta\nu_{\text{iso}}(T_0)$. We then plotted $\delta\nu_{\text{iso}}(T_0)$ as a function of laser intensity, and restricted all further analyses to those laser intensities for which $\delta\nu_{\text{iso}}(T_0)$ was intensity independent. An example of these data is shown in Fig. 3(a) for our 3.5-torr Xe cell. As illustrated in the figure, $\delta\nu_{\text{iso}}(T_0)$ was effectively independent of laser intensity for values below $10\ \mu\text{W}/\text{cm}^2$ and this procedure was performed for each Xe cell.

(ii) *Generate a first estimate of $\partial[\delta\nu]/\partial P|_{T_0}$.* Using the restricted set of low intensities, we averaged $\delta\nu_{\text{iso}}(T_0)$ over laser intensity and estimated $\partial[\delta\nu]/\partial P|_{T_0}$ by taking the ratio of this average to the Xe pressure in the cell.

(iii) *Determine the collision shift as a function of temperature.* Again restricting our attention to the set of low laser intensities, we averaged $\delta\nu_{\text{iso}}(T)$ over laser intensity for each temperature in our temperature series, creating a data set like that shown in Fig. 3(b) for the 3.5-torr Xe cell. The intercept from a linear least-squares fit of such data provided an estimate of $\delta\nu_{\text{iso}}(T_0)$ and thereby our second estimate of $\partial[\delta\nu]/\partial P|_{T_0}$. The slope from the least-squares fit provided our estimate of κ . Regarding the data of Fig. 3(b) specifically, the fact that a fairly good estimate of κ can be obtained from such a low-pressure cell over such a narrow range of temperatures is a testament to the isoclinic-point technique.

To within a 95% confidence interval there was no statistically significant difference between our first and second estimates of $\partial[\delta\nu]/\partial P|_{T_0}$; we report here our second estimates.

Figure 4(a) shows the collection of Rb D_1 collision-shift coefficients (i.e., $\partial[\delta\nu]/\partial P$) at $T_0 = 45^\circ\text{C}$ for each of our cells, where error bars correspond to 95% confidence intervals. (Unless specifically indicated, all uncertainties and error bars are 1σ .) Though visually the data appear to have a quadratic dependence on pressure, a one-way analysis of variance (ANOVA) [28] indicated that at a 95% confidence level there was no evidence of a difference among these collision-shift coefficients. Thus, taking a weighted average over the four cells in our sample [29], we obtained $\partial[\delta\nu]/\partial P|_{T_0=318\text{K}} = -(5.38 \pm 0.02)\text{ MHz/torr}$, which corresponds to a 0.4% measurement uncertainty. Similarly, Fig. 4(b) shows the collection of κ exponents for each of our cells, where error bars again correspond to 95% confidence intervals. Similar to the collision-shift coefficients, a one-way ANOVA indicated that at a 95% confidence level there was no evidence of a difference among these κ values. Taking a weighted average over the four cells in our sample, we therefore have $\kappa = 0.32 \pm 0.05$.

III. THE κ EXPONENTS AND THE FORM OF THE INTERACTION POTENTIAL

Figure 5 shows a complete set of published experimental κ exponents for the Rb and Cs D_1 transitions: *A*, Romalis *et al.* [30]; *B*, Kluttz *et al.* [31]; *C*, Kozlova *et al.* [32]; *D*, Wells *et al.* [19]; and *E*, the present work. Circles correspond to Rb, while diamonds correspond to Cs. The dashed and dash-dotted lines correspond to the only theoretical estimates of κ for Rb and

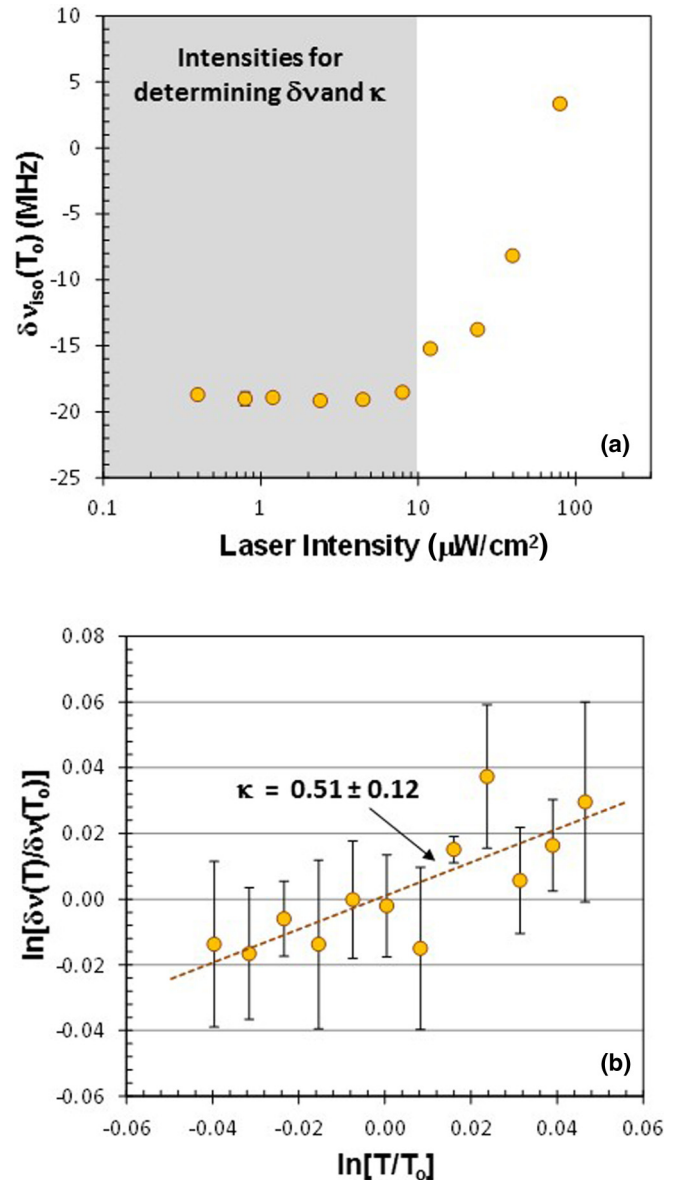


FIG. 3. (Color online) (a) Estimated collision shift in our 3.5-torr Xe cell at $T_0 = 45^\circ\text{C}$, $\delta\nu_{\text{iso}}(T_0)$, as a function of measurement-cell laser intensity. For laser intensities less than $10\ \mu\text{W}/\text{cm}^2$, $\delta\nu_{\text{iso}}(T_0)$ is independent of intensity, indicating that for those laser intensities the measurement of $\delta\nu$ is not influenced by repopulation optical pumping. (b) Averaging over laser intensities in the shaded portion of (a), this graph shows the relative change in $\delta\nu_{\text{iso}}$ as a function of temperature, where the error bars correspond to $1\text{-}\sigma$ values. The intercept of the linear fit yields our second estimate of $\partial[\delta\nu]/\partial P$, while the slope provides our estimate of κ .

Cs, respectively [3]. 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 κ exponent measurements using traditional spectroscopic techniques. Conversely, the Rb-Kr and Rb-Xe κ exponents based on isoclinic-point measurements not only are consistent with one another (as one would expect for Rb interacting with

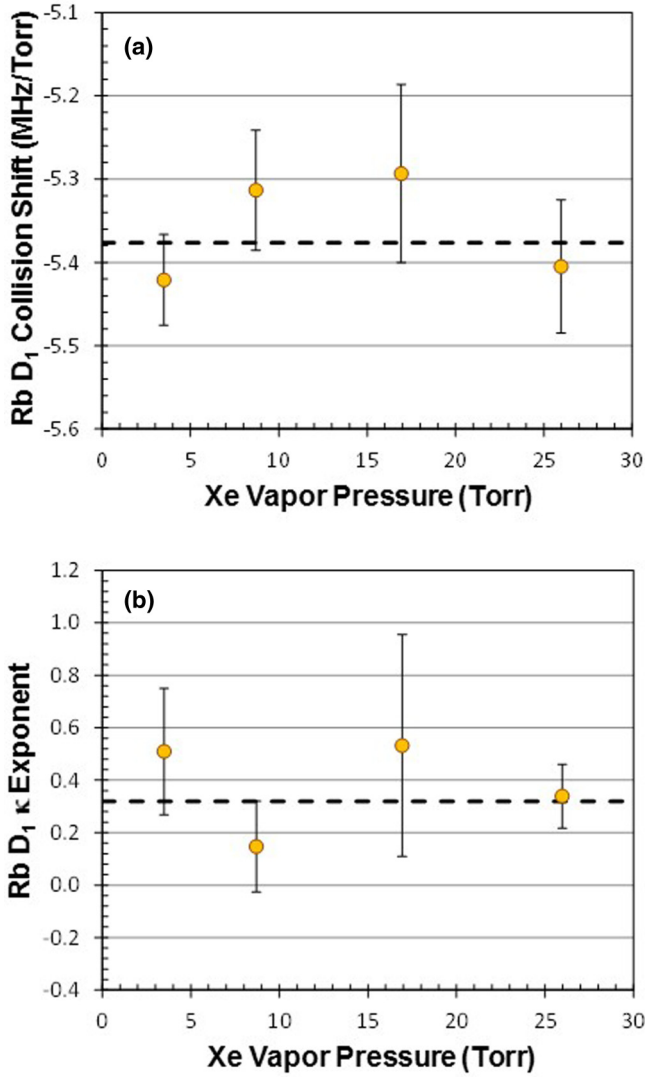


FIG. 4. (Color online) (a) The Rb-Xe collision shift coefficient (i.e., $\partial[\delta\nu]/\partial P$) as measured at different Xe pressures. The dashed line is the weighted mean. (b) The κ exponents measured at different Xe pressures. Again, the dashed line is the weighted mean.

the heavier noble gases), but agree very well with theory: $\kappa_{\text{th}} = 0.31$ [3].

Independent of simply correlating line-shift measurements at different temperatures, the κ exponent provides a somewhat unique perspective on the alkali-metal–noble-gas interaction. If we consider the very simple case of an alkali metal perturbed in its ground state $|g\rangle$ and excited state $|e\rangle$ by an interaction of the form $V(R) = C_p/R^p$, then

$$\delta\nu(T) = [D_{\text{NG}}]\beta(p)|C_{p,e} - C_{p,g}|^{2/(p-1)}T^{(p-3)/2(p-1)}, \quad (1)$$

where $[D_{\text{NG}}]$ is the noble-gas density and $\beta(p)$ is a numerical factor that depends on the power-law form of the interaction potential [8]. Consequently, the collision shift depends on the strength of the ground- and excited-state interaction potentials and the dominant power-law form of the interaction. Alternatively, Eq. (1) shows that $\delta\nu(T) \sim T^{(p-3)/2(p-1)}$. In other words, κ is a direct measure of the power-law form of the interaction potential independent of the interaction’s strength.

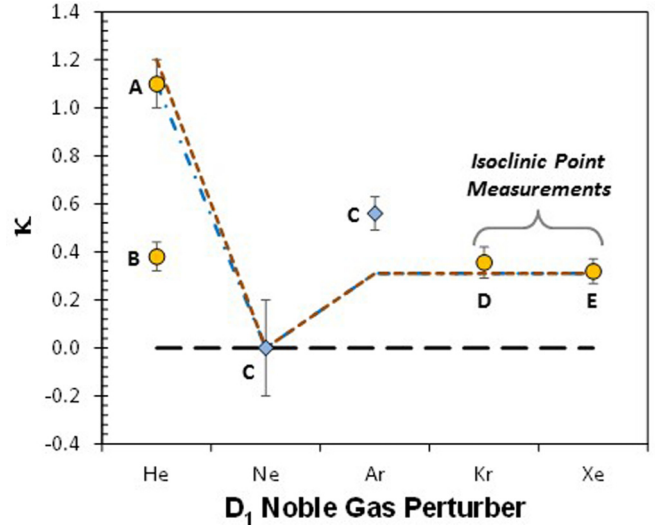


FIG. 5. (Color online) Summary of known Rb (circles) and Cs (diamonds) κ exponents for D_1 perturbation by the noble gases: A, Ref. [30]; B, Ref. [31]; C, Ref. [32]; D, Ref. [19]; and E, the present work. The dashed line corresponds to theory for Rb and the dash-dotted line theory for Cs [3].

In particular, as illustrated in Fig. 6, a measurement of κ can provide an independent constraint on the power-law form of the ground-state–excited-state difference potential. In the case of Rb perturbed by the heavy noble gases, the theoretical value of κ (i.e., $\kappa_{\text{th}} = 0.31$) is well supported by the experimental results and thereby the experimental κ exponents provide independent evidence for $[V_e(R) - V_g(R)]$ having something very close to a $1/R^6$ form.

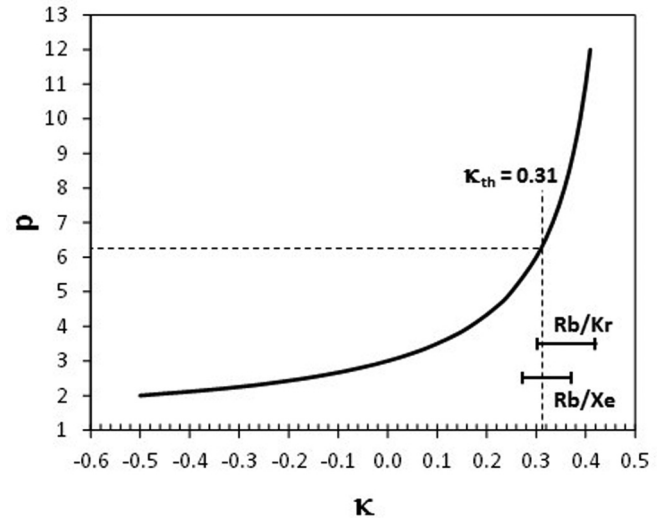


FIG. 6. Assuming that the ground and excited states of an alkali-metal atom interact with a noble-gas atom primarily via a $1/R^p$ potential, this curve shows p as a function of the κ exponent (i.e., $\delta\nu \sim T^\kappa$). The theoretical value of 0.31 (well supported by the experimental results) indicates that the Rb and Cs interactions with the heavy noble gases are primarily influenced by an interaction that varies with distance like $1/R^6$: a van der Waals interaction. Error bars correspond to 1σ .

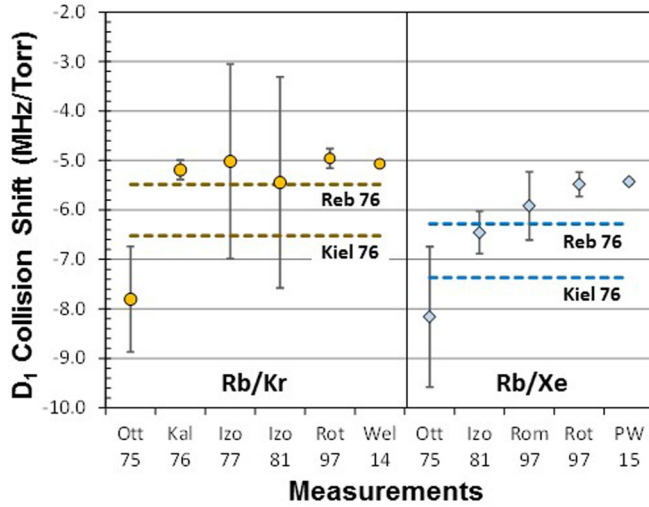


FIG. 7. (Color online) Comparison of theory and experiment for the D_1 Rb collision shift by Kr and Xe: Ott 75, Ref. [33]; Kal 76, Ref. [21]; Izo 77, Ref. [34]; Izo 81, Ref. [35]; Rot 97, Ref. [20]; Wel 14, Ref. [19]; Rom 97, Ref. [30]; PW 15, the present work; Reb 76, Ref. [4]; and Kiel 76, Ref. [3]. Error bars correspond to 95% confidence intervals.

IV. DISCUSSION

Figure 7 is a summary of the experimental situation regarding the collision shift of the Rb D_1 line by Kr and Xe, where we have employed our isoclinic-point assessments of κ to bring all collision-shift measurements to the same temperature: $T = 323$ K. (Error bars include the 95% confidence intervals and the individual measurement errors as well as the error associated with our determination of κ .) The dashed lines correspond to two theoretical calculations of the D_1 collision shift. Rebane's [4] calculation is carried out at 323 K and therefore is directly comparable to the experimental results. Kielkopf's [3] calculation is carried out at 500 K, but κ is also computed by Kielkopf allowing theoretical extrapolation to 323 K.

Clearly, over the past years there has been a narrowing of the experimental uncertainty regarding the D_1 collision shift [21,33–35]. Specifically, the most recent measurements for the Rb-Kr system by Rotondaro and Perram [20] and the present authors [19] are in excellent agreement, as are the most recent measurements by the two groups for the Rb-Xe system. Moreover, it is important to note that our results and those of Rotondaro and Perram represent two very distinct approaches to measuring $\delta\nu$: Rotondaro and Perram employ 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 the Rotondaro and Perram results, or equivalently our results, it is hard to imagine a systematic effect that would influence both approaches in the same way and to the same extent. Combining the two groups' results by taking a simple average, accounting for uncertainty by pooling the two groups' variances [36], we therefore have for the Rb D_1 collision shift (in MHz/torr)

$$\left. \frac{\partial[\delta\nu]}{\partial P} \right|_{T=323\text{ K}} = \begin{cases} -5.02 \pm 0.07 & \text{for Kr} \\ -5.46 \pm 0.09 & \text{for Xe.} \end{cases} \quad (2)$$

As discussed in the previous section, the experimental κ exponents indicate that (not surprisingly) the Rb-heavy-noble-gas interaction is dominated by a $1/R^6$ van der Waals potential. Thus, Eq. (1) should provide a fairly good approximation to the collision shift and thereby a fairly simple expression for the ratio of the Rb-Xe to Rb-Kr shifts. Specifically, taking $C_{p,g}/C_{p,e}$ as roughly constant for an alkali metal interacting with any of the heavy noble gases, we have

$$\frac{\delta\nu_{\text{Rb-Xe}}}{\delta\nu_{\text{Rb-Kr}}} \approx \left(\frac{C_{p,\text{Rb-Xe}}}{C_{p,\text{Rb-Kr}}} \right)^{2/(p-1)} \approx \left(\frac{\varepsilon_{\text{Xe}}(\varepsilon_{\text{Rb}} + \varepsilon_{\text{Kr}}) \alpha_{\text{Xe}}}{\varepsilon_{\text{Kr}}(\varepsilon_{\text{Rb}} + \varepsilon_{\text{Xe}}) \alpha_{\text{Kr}}} \right)^{2/5}, \quad (3)$$

The last term on the right-hand side of Eq. (3) is an approximate expression for the dispersion force constant ($p = 6$) as discussed by Margenau [37], with ε the ionization potential and α the polarizability [38]. Note that this ratio is temperature independent, depending only on the relative strengths of the van der Waals interaction. Defining Eq. (3) as the approximate ratio of line shifts, we have

$$\frac{\delta\nu_{\text{Rb-Xe}}}{\delta\nu_{\text{Rb-Kr}}} = 1.20, \quad (4a)$$

$$\frac{\delta\nu_{\text{Rb-Xe}}}{\delta\nu_{\text{Rb-Kr}}} = 1.09 \pm 0.02, \quad (4b)$$

$$\frac{\delta\nu_{\text{Rb-Xe}}}{\delta\nu_{\text{Rb-Kr}}} = 1.15, \quad (4c)$$

$$\frac{\delta\nu_{\text{Rb-Xe}}}{\delta\nu_{\text{Rb-Kr}}} = 1.13 \quad (4d)$$

for the approximate, experimental, Rebane, and Kielkopf results, respectively. In general, Eqs. (4) are all very consistent, indicating a relatively small (i.e., 10%–15%) increase in the difference potential going from Kr to Xe. Though the experimental and theoretical values of the ratio are all less than the approximation, this is likely a simple reflection of the approximations involved in Eq. (3).

Notwithstanding the consistency between theory and experiment regarding the ratio of Rb-Xe to Rb-Kr collision shifts, the experimental situation does suggest that something is lacking in theory. As illustrated in Fig. 7, both Rebane and Kielkopf overestimate the collision shifts for the Rb-Kr and Rb-Xe systems. While Kielkopf's modeling of the interaction potential is more detailed than Rebane's (as Kielkopf considers a quadrupole $1/R^8$ term in the potential [2]), Rebane's theory explicitly accounts for the fine and hyperfine structure of the alkali metal. Though the difference between theory and experiment is not large, it is nonetheless statistically significant (i.e., roughly 20%). In particular, since both theories determine the magnitude of the van der Waals ground and excited-state coefficients in a similar fashion, and since the alkali-metal ground state's interaction with the noble gases is arguably better understood than the excited-state interaction, it would appear that there is a need for a closer theoretical examination of the noble-gas atom's interaction with the alkali metal $^2P_{1/2}$ state.

V. SUMMARY

In this work we have measured the Rb D_1 collision shift by Xe using the ^{87}Rb isoclinic point. Not only has this allowed

us to measure the exponent in the collision shift's dependence on temperature κ , which is a measure of the power-law form of the alkali-metal–noble-gas interaction potential, but it has provided a measurement of the collision-shift coefficient (i.e., $\partial[\delta\nu]/\partial P$) that has an uncertainty of only 0.4%. With this precision, coupled with the ability to use κ to translate diverse experimental and theoretical results to the same temperature, we were able to test theory to something close to this level of accuracy. Comparing best estimates of the D_1 collision shift for the Rb-Kr and Rb-Xe systems to theory, we find evidence of a theoretical discrepancy on the order of 20%. On the one hand, this represents fairly good agreement between theory and experiment, and indicates that the overarching features of the alkali-metal–noble-gas interaction are well understood (at least regarding the heavier noble gases). On the other hand, however, it suggests room for improvement. While our initial

suspicion is that the discrepancy lies with the van der Waals coefficient describing the $1/R^6$ interaction of the noble-gas atom with the alkali-metal $^2P_{1/2}$ state, we recognize that an explanation for the discrepancy could eventually be found elsewhere (e.g., elastic fine-structure mixing collisions [27]). To help resolve this issue, collision-shift measurements with the lighter noble gases might prove informative.

ACKNOWLEDGMENTS

We thank M. Huang for his assistance in setting up our pressure measurement system. This work was supported by The Aerospace Corporation's Sustained Experimentation and Research for Program Applications program and funded by U.S. Air Force Space and Missile Systems Center under Contract No. FA8802-09-C-0001.

-
- [1] T. M. Miller and B. Bederson, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and B. Bederson (Academic, New York, 1977), Vol. 13, pp. 1–55.
- [2] J. F. Kielkopf, Semiempirical potentials for alkali-noble gas interactions, *J. Chem. Phys.* **61**, 4733 (1974).
- [3] F. Kielkopf, Predicted alkali collision broadening by noble gases based on semiempirical potentials, *J. Phys. B* **9**, L547 (1976).
- [4] V. N. Rebane, Calculation of the broadening and shift of hyperfine components of rubidium and cesium D_1 lines in collisions with atoms of heavy inert gases, *Opt. Spectrosc.* **41**, 526 (1976).
- [5] E. S. Hryciyshyn and L. Krause, Inelastic collisions between excited alkali atoms and molecules. VII. Sensitized fluorescence and quenching in mixtures of rubidium with H_2 , HD, D_2 , N_2 , CH_4 , CD_4 , C_2H_4 , and C_2H_6 , *Can. J. Phys.* **48**, 2761 (1970).
- [6] N. D. Zameroski, W. Rudolph, G. D. Hager, and D. A. Hostutler, A study of collisional quenching and radiation-trapping kinetics for Rb($5p$) in the presence of methane and ethane using time-resolved fluorescence, *J. Phys. B* **42**, 245401 (2009).
- [7] J. F. Kielkopf, On the precise evaluation of the complete semiclassical spectral line shape for pressure-broadened atomic spectra lines, *J. Phys. B* **9**, 1601 (1976).
- [8] G. Peach, Theory of the pressure broadening and shift of spectral lines, *Adv. Phys.* **30**, 367 (1981).
- [9] Y. Liu, J. Lin, G. Huang, Y. Guo, and C. Duan, Simple empirical analytical approximation to the Voigt profile, *J. Opt. Soc. Am.* **18**, 666 (2001).
- [10] J. H. Eberly, Atomic Relaxation in the Presence of Intense Partially Coherent Radiation Fields, *Phys. Rev. Lett.* **37**, 1387 (1976).
- [11] J. C. Camparo and P. Lambropoulos, Monte Carlo simulation of field fluctuations in strongly driven resonant transitions, *Phys. Rev. A* **47**, 480 (1993).
- [12] Y. Sun and C. Zhang, Stochasticity in narrow transitions induced by laser noise, *Phys. Rev. A* **89**, 032516 (2014).
- [13] P. Zoller and P. Lambropoulos, Non-Lorentzian laser line-shapes in intense field-atom interaction, *J. Phys. B* **12**, L547 (1979).
- [14] G. A. Pitz, D. E. Wertepny, and G. P. Perram, Pressure broadening and shift of the cesium D_1 transition by the noble gases and N_2 , H_2 , HD, D_2 , CH_4 , C_2H_6 , CF_4 , and 3He , *Phys. Rev. A* **80**, 062718 (2009).
- [15] G. A. Pitz, A. J. Sandoval, T. B. Tafoya, W. L. Klennert, and D. A. Hostutler, Pressure broadening and shift of the rubidium D_1 transition and potassium D_2 transitions by various gases with comparison to other alkali rates, *J. Quant. Spectrosc. Radiat. Transfer* **140**, 18 (2014).
- [16] P. Siddons, C. S. Adams, C. Ge, and I. G. Hughes, Absolute absorption on rubidium D lines: Comparison between theory and experiment, *J. Phys. B* **41**, 155004 (2008).
- [17] N. P. Wells and J. C. Camparo, ^{87}Rb D_1 isoclinic point, *Phys. Rev. A* **82**, 062505 (2010).
- [18] *IUPAC. Compendium of Chemical Terminology*, 2nd ed., compiled by A. D. McNaught and A. Wilkinson (Blackwell, Oxford, 1997); M. Nic, J. Jirat, and B. Kosata, XML online corrected version available at <http://goldbook.iupac.org> (2006), updates compiled by A. Jenkins.
- [19] N. P. Wells, T. U. Driskell, and J. C. Camparo, Kr-collision shift of the Rb D_1 transition: The isoclinic point and precision optical spectroscopy, *Phys. Rev. A* **89**, 052516 (2014).
- [20] M. D. Rotondaro and G. P. Perram, Collisional broadening and shift of the rubidium D_1 and D_2 lines ($5^2S_{1/2} \rightarrow 5^2P_{1/2}, 5^2P_{3/2}$) by rare gases, H_2 , D_2 , N_2 , CH_4 and CF_4 , *J. Quant. Spectrosc. Radiat. Transfer* **57**, 497 (1997).
- [21] N. I. Kaliteevskii, O. M. Rish, and M. P. Chaika, Measurement of the broadening and shift of the D_1 line of rubidium 87 due to collision with atomic krypton, *Opt. Spectrosc.* **41**, 293 (1976).
- [22] S. A. Kazantsev, G. M. Smirnova, and V. I. Khutorshchikov, Radiospectroscopic method for precision measurement of gas pressure, *Opt. Spectrosc.* **80**, 10 (1996).
- [23] J. Camparo, The rubidium atomic clock and basic research, *Phys. Today* **60**(11), 33 (2007).
- [24] J. Vanier, R. Kunski, N. Cyr, J. Y. Savard, and M. Têtu, On hyperfine frequency shifts caused by buffer gases: Application to the optically pumped passive rubidium frequency standard, *J. Appl. Phys.* **53**, 5387 (1982).
- [25] T. U. Driskell, M. Huang, and J. C. Camparo, in *Proceedings of the 2015 Joint IEEE International Frequency Control*

- Symposium and 29th European Frequency and Time Forum* (IEEE, Piscataway, 2015), pp. 474–479.
- [26] In Ref. [19], examining the collision shift of the Rb D_1 line by Kr, we noted a systematic shift in our isoclinic point measurements that appeared to correspond to one time step of our averaging oscilloscope. In the present Xe measurements, we found no evidence for this systematic shift. Consequently, in the Kr result reported here we decided to remove this systematic *correction* from our previous Kr result and replace it with a systematic *uncertainty* in krypton's reported collision-shift value.
- [27] N. P. Wells, T. U. Driskell, and J. C. Camparo, Fine-structure mixing in Rb-Xe elastic collisions and isoclinic point asymmetry, *Phys. Rev. A* **92**, 022505 (2015).
- [28] H. Robbins and J. Van Ryzin, *Introduction to Statistics* (Science Research Associates, Chicago, 1975), Chap. 8.
- [29] W. G. Cochran, The combination of estimates from different experiments, *Biometrics* **10**, 101 (1954).
- [30] M. V. Romalis, E. Miron, and G. D. Cates, Pressure broadening of Rb D_1 and D_2 lines by ^3He , ^4He , N_2 , and Xe: Line cores and near wings, *Phys. Rev. A* **56**, 4569 (1997).
- [31] K. A. Kluttz, T. D. Averett, and B. A. Wolin, Pressure broadening and frequency shift of the D_1 and D_2 lines of Rb and K in the presence of ^3He and N_2 , *Phys. Rev. A* **87**, 032516 (2013).
- [32] O. Kozlova, S. Guérandel, and E. de Clercq, Temperature and pressure shift of the Cs clock transition in the presence of buffer gases: Ne, N_2 , and Ar, *Phys. Rev. A* **83**, 062714 (2011).
- [33] C. Ottinger, R. Scheeps, G. W. York, and A. Gallagher, Broadening of the Rb resonance lines by the noble gases, *Phys. Rev. A* **11**, 1815 (1975).
- [34] S. L. Izotava, A. I. Kantserov, and M. S. Frish, Measurement of the shift and broadening of STS components of a rubidium line in the presence of krypton, *Opt. Spectrosc.* **42**, 120 (1977).
- [35] S. L. Izotava, A. I. Kantserov, and M. S. Frish, Constants for broadening and shift of D_1 and D_2 rubidium-87 lines by inert gases, *Opt. Spectrosc.* **51**, 107 (1981).
- [36] A. Hald, *Statistical Theory with Engineering Applications* (Wiley, New York, 1952), Chap. 11.
- [37] H. Margenau, Van der Waals forces, *Rev. Mod. Phys.* **11**, 1 (1939).
- [38] T. M. Miller and B. Bederson, in *Advances in Atomic and Molecular Physics* (Ref. [1]), p. 1.