# Pressure shifts and broadenings of Rb Rydberg states by Ne, Kr, and $H_2$

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Broadening and shift rates for Rb $^2S$ and $^2D$ Rydberg states with principal quantum number $n \sim 10-50$ have been measured for Ne, Kr, and $H_2$ perturbers, using the technique of Doppler-free two-photon spectroscopy. From the shift rates at high $n$, we derived electron scattering lengths of $(0.24\pm0.01)a_0$ for Ne, $(-4.0\pm0.3)a_0$ for Kr, and $(1.64\pm0.07)a_0$ for $H_2$. For Ne and Kr, these are in good agreement with other experimental values. Also, the $n$ dependence of broadening and shift rates follows theoretical predictions for Ne and Kr, but not for $H_2$.

## I. INTRODUCTION

Measurements of changes in atomic absorption lines due to collisions with other atoms or molecules are of interest because of the relationship between these changes—particularly broadenings and frequency shifts and the dynamics of the collisions. Studies of shifts and broadenings of absorption lines involving alkali-metal atoms in Rydberg states[1–4] have been of special interest because the large separations between Rydberg electrons and ionic cores simplify theoretical descriptions of collisions. The theory for pressure shifts originates with Fermi[5] and has more recently been extended by Alekseev and Sobel'man[6] to include broadening, and by Omont[7] and Kaulakys[8] to give the dependence of broadening and shift on principal quantum number $n$.

Early experiments[1–3] with Doppler-broadened spectra required high perturber pressures. Recently, however, the use of lasers and sensitive thermionic detection[9] in Doppler-free two-photon spectroscopy[10–12] (DFTPS) has allowed studies of pressure shift and broadening of Rydberg states at pressures $<1$ Torr.[4,13–16] Under these conditions only binary collisions are important and the impact approximation[17] holds. This work continues a series of studies in this laboratory using DFTPS to study the $^2S$ and $^2D$ Rydberg states in alkali-metal atoms[9,18] and the broadening and shift of spectral lines due to collisions with ground-state atomic perturbers.[14,16] Here we investigate the shifts and broadenings of spectra arising from transitions $n\,^2S \leftarrow 5\,^2S$ and $n\,^2D \leftarrow 5\,^2S$, for $n=10-50$, in Rb at low pressure perturbed by the rare gases Ne and Kr, as well as by molecular hydrogen. These perturbers were selected in order to make comparisons with results from electron scattering experiments and to complement similar studies by Weber and Niemax[15] for He, Ar, and Xe perturbers.

## II. EXPERIMENTAL DETAILS

The experimental arrangement, including rubidium sample cells, tunable lasers, and associated optics was similar to that used in the earlier studies of alkali-metal pressure shifts and broadenings,[14,16] and is shown in Fig. 1.

In each experiment, two rubidium cells were used—a reference cell at a constant Rb pressure, and a "pressure" cell fitted with a valve to allow the foreign-gas pressure to be changed. In this way frequency shifts as well as broadenings of lines could be studied. The cells were of Pyrex and contained a thermionic detector[9] centered between two optical quality windows. Each cell was enclosed in a two-chamber oven so that the body of the cell could be maintained at a higher temperature ($\sim 530$ K) than the sidearm containing the liquid rubidium ($\sim 420-460$ K). This ensured control of vapor pressure and prevented condensation of rubidium metal on the windows. The cells were baked and evacuated to $10^{-7}$ Torr, then charged with $\sim 1$ g of Rb. The Rb metal (from Ventron) was specified as 99.95% pure, with much of the balance being Cs. This impurity was further reduced (before sealing of the cell) by heating the cell and sidearm to $>200\,^\circ$C for several hours while condensing any vapors in an auxiliary cold trap. Temperatures of the sidearm and main body for each cell were measured using copper-constantan thermocouples. The Rb vapor pressure was determined from the relation given by Nesmeyanov.[19] Krypton pressures were measured with $\sim 5\%$ precision using a Pirani-type gauge. A Bourdon gauge was used for measuring Ne and $H_2$ pressures to $\sim 2\%$, as well as for calibrating the earlier Kr pressures.

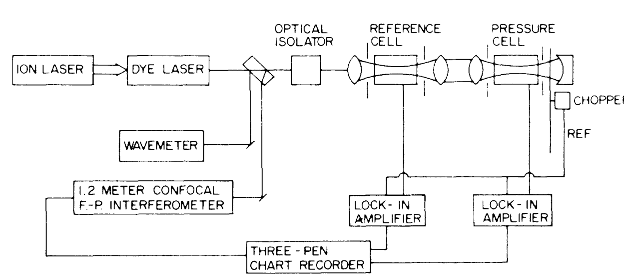


FIG. 1. Schematic diagram of experimental apparatus.

 

Tunable laser radiation for excitation of the spectra was provided by a stabilized dye laser (Coherent model 599-21) using R6G dye, pumped by either a krypton-ion laser (Coherent model 3000K) or an argon-ion laser (Coherent model CR-3). Up to 150 mW of single-mode cw output was produced, with a frequency jitter of $\sim 1-3$ MHz. This radiation was transmitted through an optical isolator (a Faraday rotator and a Glan-Thompson polarizer), focused into the reference cell and recollimated, then focused into the "pressure" cell, and finally reflected back on itself with a concave mirror. The reflected beam was chopped to allow synchronous detection of the Doppler-free signal.

Small portions of the dye-laser beam were directed to a wavemeter[20] for location of transitions at known wavelengths,[18] and to a 1.2-m confocal Fabry-Perot interferometer to provide a frequency scale for measurements of linewidths and shifts. The interferometer was calibrated against the ground-state hyperfine splitting of the two-photon spectrum of Cs, giving a free-spectral range of $124.91 \pm 0.08$ MHz.

Spectra from the pressure and reference cells, together with transmission peaks of the Fabry-Perot interferometer were recorded simultaneously on a three-pen chart recorder. The rubidium vapor pressure in both reference and "pressure" cells was kept approximately constant at a value of a few mTorr, while the pressure of foreign gas in the pressure cell was varied. At each pressure, the dye laser was successively tuned to each of the Rydberg transitions to be studied. From three to ten scans (of $\sim 5$-min duration) of each spectrum were recorded and the results averaged. Frequency shifts were measured between the centers of the pressure and reference lines, and measured linewidths were the full widths at half maximum (FWHM) intensity. Corrections amounting to a few MHz at most were made for laser jitter, instrumental time constant, and transit time broadening.[21] Broadenings or shifts of lines due to stray electric or magnetic fields or high laser powers were estimated to be $< 1$ MHz.

## III. RESULTS

The spectra for $n\,^2S \leftarrow 5\,^2S$ transitions show four components arising from the two isotopes $^{85}$Rb and $^{87}$Rb, and from the hyperfine splittings of the corresponding ground states. Scans of the strongest components, $n\,^2S_{1/2} \leftarrow 5\,^2S_{1/2}$ $(F=3)$ in $^{85}$Rb were recorded for measurement. Due to the fine-structure splittings of excited $^2D$ states, the $^2D$ spectra show eight components. Again, the strongest transitions, $n\,^2D_{5/2} \leftarrow 5\,^2S_{1/2}$ $(F=3)$, were scanned. In the $16\,^2D$ and $17\,^2D$ spectra, because of overlapping of several components, the spectra of $n\,^2D_{3/2} \leftarrow 5\,^2S_{1/2}$ $(F=3)$ were studied instead. For each spectrum the scanned component was well separated from its neighbors so that even at the highest pressures only a very small correction for overlap was required. No asymmetry was detected for any of the measured line profiles. Also, there was no evidence of background absorption by $Rb_2$ molecules (vapor pressure $\sim 10^{-3}$ times that of Rb) in any of the observed spectra.

After correction for Rb self-broadening and shift using previously measured rates,[16] linewidths and shifts showed the expected linear dependence of foreign-gas pressure.

### A. Krypton

Measurements were made at krypton pressures of 0, 63, 111, and 270 mTorr and a cell temperature of $\sim 530$ K. The spectra involving the states $10\,^2S$ to $35\,^2S$, $37\,^2S$, $40\,^2S$, $9\,^2D$ to $35\,^2D$, $37\,^2D$, $40\,^2D$, $45\,^2D$, and $50\,^2D$ were studied at 0 and 63 mTorr. In addition, spectra of states $10^2S$ to $26\,^2S$, $30\,^2S$, $35\,^2S$, $40\,^2S$, $9\,^2D$ to $15\,^2D$, and every fifth state from $20\,^2D$ to $50\,^2D$ were studied at one or both of the higher pressures. The observed shifts were to lower frequencies.

Our measured rates for shifts and broadenings are listed in Table I and shown in Figs. 2 and 3, respectively. For both $^2S$ and $^2D$ series, the $n$ dependence of broadening and shift rates is similar to that observed in other work with rare-gas perturbers. The broadenings rates increase to a maximum at $n^* \sim 10$, and decrease for higher $n$. The shift rates increase with $n$ and level off for $n^* > 15$. There is little difference between the results for the $^2S$ and $^2D$ series. In particular, the shift rates for large $n$ agree for the two series, as do the maximum broadening rates. The asymptotic (large $n$) shift rate is $490 \pm 30$ MHz/Torr, corresponding to a cross section of $(3.3 \pm 0.2) \times 10^{-12}$ cm$^{-2}$. The peak broadening rate at $n^* \sim 10$ is $\sim 400$ MHz/Torr, corresponding to a cross section of $\sim 1.3 \times 10^{-12}$ cm$^2$, while the asymptotic broadening rate of $80 \pm 10$ MHz/Torr gives a cross section of $(2.7 \pm 0.3) \times 10^{-13}$ cm$^2$.

### B. Neon

Measurements were made at neon pressures of 1.9, 3.7, and 11.2 Torr and a cell temperature of $\sim 525$ K. In the $^2S$ series, spectra involving states with $n = 14$, 17, 20, 25, 30, and 35 were studied at each of these pressures, as were spectra of $^2D$ states with $n = 14$, 17, 20, 25, and 30. Shift and broadening rates for each of these states are listed in Table I and shown in Figs. 2 and 3, respectively. The observed shifts are to higher frequencies for neon.

For neon, the broadening and shift rates are the same for both series. Broadening rates are essentially independent of $n$, for the range of $n$ values studied; however, in contrast to krypton, the shift rates decrease slightly with increasing $n$. For large $n$, the shift rate is constant at $12 \pm 1$ MHz/Torr, corresponding to a cross section of $(5.0 \pm 0.4) \times 10^{-14}$ cm$^2$. The broadening rate of $17 \pm 1$ MHz/Torr at large $n$ gives a cross section of $(3.5 \pm 0.2) \times 10^{-14}$ cm$^2$.

While the data of Figs. 2 and 3 give the overall behavior on principal quantum number, measurements of widths and shifts were also made at each value of $n$ from 12–40 for spectra of the $^2S$ and $^2D$ series (but only at a neon pressure of 1.9 Torr) in order to look for possible oscillations in their dependence on $n$. These measurements are plotted versus $n$, in Fig. 4. The data are essentially constant with $n$, and reveal no evidence of oscillations in widths or shifts with $n$ for either series.

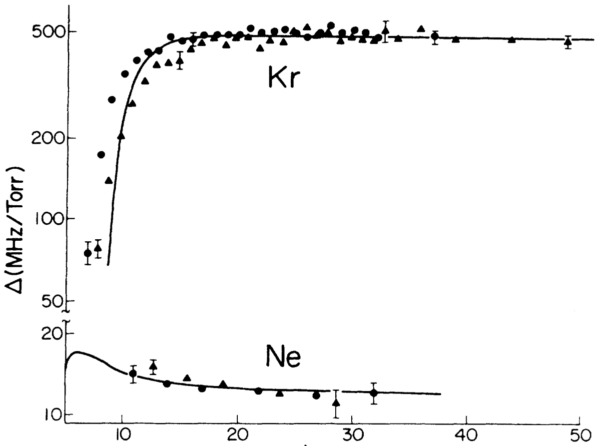


FIG. 2. Experimental shift rates for Rb $^2S$ (●) and $^2D$ (▲) states perturbed by Kr and Ne. The shift rates calculated according to Eq. (3) are given by the solid lines.

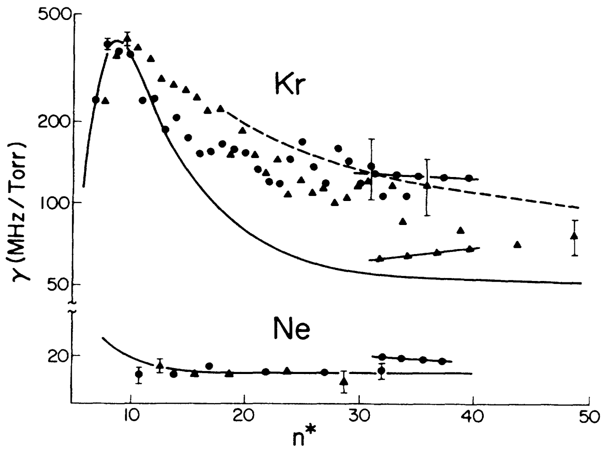


FIG. 3. Experimental broadening rates for Rb $^2S$ (●) and $^2D$ (▲) states perturbed by Kr and by Ne. Also shown for comparison are the rates calculated from Eq. (2a) (——), from Eqs. (2a) and (4) (— — —), and from Eq. (2a) plus the results of Ref. 36 for $^2S$ (—●—) and for $^2D$ (—▲—) states, available at $n^* \sim 30$–40.

TABLE I. Shift and broadening rates (in MHz/Torr) for Rb $^2S$ and $^2D$ states perturbed by Ne, Kr, and $H_2$.

| | Ne | | Kr | | $H_2$ | |
|---|---|---|---|---|---|---|
| State | $\Delta^a$ | $\gamma^b$ | $\Delta$ | $\gamma$ | $\Delta$ | $\gamma$ |
| 10*S* | | | −75±10 | 240±45 | | |
| 11*S* | | | −175±10 | 385±20 | | |
| 12*S* | | | −280±15 | 360±30 | | |
| 13*S* | | | −350±15 | 350±20 | | |
| 14*S* | 14.1±1.1 | 17.0±1.2 | −390±20 | 235±30 | 105±5 | 77±3 |
| 15*S* | | | −420±40 | 240±25 | 110±5 | 78±3 |
| 16*S* | | | −425±20 | 185±15 | 120±5 | 80±3 |
| 17*S* | 12.6±0.8 | 16.9±0.9 | −475±25 | 205±20 | 110±5 | 78±3 |
| 18*S* | | | −460±30 | 175±20 | 125±5 | 76±5 |
| 19*S* | | | −470±25 | 150±20 | 130±5 | 75±4 |
| 20*S* | 12.3±0.8 | 18.2±1.1 | −485±25 | 155±15 | 135±5 | 76±5 |
| 21*S* | | | −490±30 | 165±20 | 135±5 | 74±4 |
| 22*S* | | | −490±30 | 155±25 | 140±5 | 74±4 |
| 23*S* | | | −495±30 | 155±20 | 140±5 | 73±3 |
| 24*S* | | | −515±30 | 130±20 | 140±5 | 64±3 |
| 25*S* | 12.2±0.8 | 17.3±0.9 | −495±25 | 120±10 | 145±5 | 66±3 |
| 26*S* | | | −505±35 | 115±15 | 145±5 | 67±4 |
| 27*S* | | | −515±45 | 145±25 | 145±5 | 64±3 |
| 28*S* | | | −500±60 | 170±50 | 145±5 | 62±3 |
| 29*S* | | | −480±45 | 135±30 | 145±5 | 63±3 |
| 30*S* | 11.6±1.1 | 17.3±1.1 | −500±30 | 115±15 | 150±5 | 65±4 |
| 31*S* | | | −535±55 | 160±35 | 155±5 | 66±3 |
| 32*S* | | | −505±50 | 140±40 | 150±10 | 60±6 |
| 33*S* | | | −515±70 | 115±40 | 145±5 | 63±5 |
| 34*S* | | | −500±50 | 140±35 | 145±5 | 58±5 |
| 35*S* | 12.1±1.1 | 17.7±1.2 | −480±25 | 105±15 | 150±5 | 60±3 |
| 36*S* | | | | | 150±5 | 59±3 |
| 37*S* | | | | | 150±5 | 59±4 |
| 40*S* | | | −485±30 | 105±25 | 155±5 | 60±4 |
| 45*S* | | | | | 155±10 | 52±8 |
| 50*S* | | | | | 155±5 | 52±5 |
| 55*S* | | | | | 155±5 | 55±5 |

TABLE I. (*Continued*).

| State | Ne $\Delta$[a] | Ne $\gamma$[b] | Kr $\Delta$ | Kr $\gamma$ | $H_2$ $\Delta$ | $H_2$ $\gamma$ |
|---|---|---|---|---|---|---|
| 9*D* | | | 80±10 | 235±15 | | |
| 10*D* | | | 140±10 | 350±20 | | |
| 11*D* | | | 205±10 | 400±25 | | |
| 12*D* | | | 270±15 | 375±20 | 125±5 | 67±3 |
| 13*D* | | | 325±15 | 335±20 | 125±15 | 66±15 |
| 14*D* | 15.0±0.9 | 18.2±1.1 | 375±25 | 285±25 | 130±5 | 68±4 |
| 15*D* | | | 380±15 | 270±15 | 130±5 | 63±3 |
| 16*D* | | | 390±30 | 260±35 | 135±5 | 64±3 |
| 17*D* | 13.5±1.2 | 17.0±1.2 | 430±30 | 245±35 | 135±5 | 63±4 |
| 18*D* | | | 455±30 | 215±35 | 140±5 | 68±4 |
| 19*D* | | | 470±30 | 220±35 | 145±5 | 65±4 |
| 20*D* | 12.9±0.8 | 16.9±1.1 | 445±20 | 150±10 | 140±5 | 65±3 |
| 21*D* | | | 475±45 | 185±45 | 140±5 | 68±4 |
| 22*D* | | | 480±35 | 150±30 | 140±5 | 65±4 |
| 23*D* | | | 435±45 | 125±35 | 145±5 | 62±4 |
| 24*D* | | | 470±40 | 145±30 | 145±5 | 60±5 |
| 25*D* | 11.9±0.8 | 17.4±1.1 | 460±25 | 105±15 | 145±20 | 67±20 |
| 26*D* | | | 505±50 | 120±35 | 145±5 | 62±5 |
| 27*D* | | | 530±50 | 105±30 | 150±5 | 60±4 |
| 28*D* | | | 490±40 | 110±25 | 145±5 | 62±4 |
| 29*D* | | | 500±45 | 100±30 | 145±5 | 63±4 |
| 30*D* | 11.0±1.3 | 16.1±1.5 | 460±25 | 105±10 | 150±5 | 60±4 |
| 31*D* | | | 485±45 | 115±30 | 150±5 | 60±5 |
| 32*D* | | | 475±45 | 120±35 | 150±5 | 60±4 |
| 33*D* | | | 470±65 | 105±30 | 150±5 | 62±3 |
| 34*D* | | | 515±50 | 115±25 | 155±5 | 60±4 |
| 35*D* | | | 480±25 | 85±55 | 150±5 | 60±4 |
| 36*D* | | | | | 155±5 | 55±4 |
| 37*D* | | | 520±50 | 115±30 | 150±5 | 65±5 |
| 38*D* | | | | | 150±5 | 60±4 |
| 39*D* | | | | | 150±5 | 57±4 |
| 40*D* | | | 475±25 | 80±10 | 150±5 | 57±3 |
| 45*D* | | | 480±25 | 70±10 | 145±10 | 51±7 |
| 50*D* | | | 470±25 | 75±10 | | |

[a]Frequency-shift rates.
[b]Broadening rates.

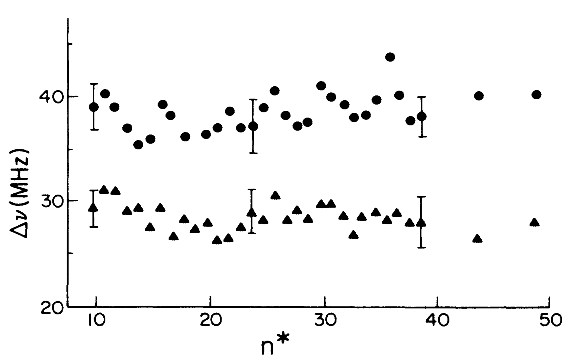


FIG. 4. Experimental linewidths (●) and frequency shifts (▲) for Rb $^2D$ states perturbed by Ne at 1.9 Torr.

### C. Hydrogen

Measurements with $H_2$ were made at a pressure of 0.75 Torr and a cell temperature of $\sim$525 K. For the $^2S$ series, spectra were recorded for $n=14$ to 37, and $n=40$, 45, 50, 55 and for the $^2D$ series, for $n=12$ to 40 and $n=45$. The observed shifts are to higher frequencies. The shift and broadening rates obtained from these measurements at only one pressure are listed in Table I and plotted in the graphs of Fig. 5. There are only small differences between the results for the $^2S$ and $^2D$ series, mainly at low $n$ values. For both series, the shifts slowly increase and reach an asymptotic value for $n>40$ of 150±9 MHz/Torr, corresponding to a cross section of $(2.16\pm0.13)\times10^{-13}$ cm$^2$. The broadening appears to decrease somewhat, giving an asymptotic broadening rate of 54±7 MHz/Torr. This corresponds to a cross section of $(3.9\pm0.5)\times10^{-14}$ cm$^2$.

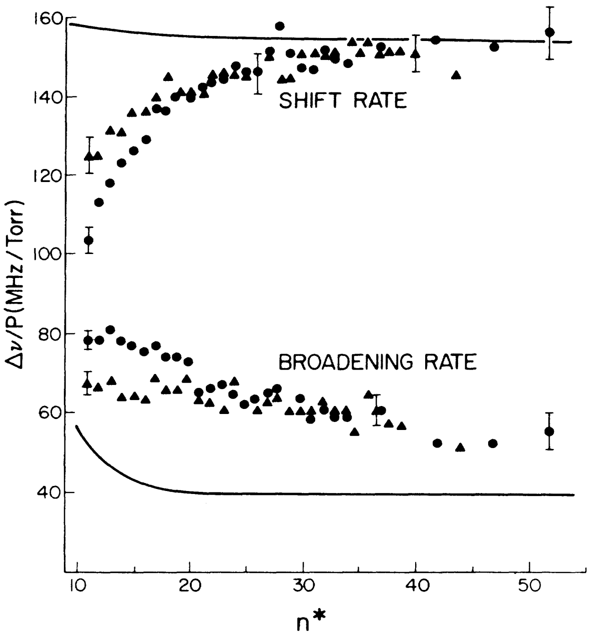


FIG. 5. Experimental shift and broadening rates for Rb $^2S$ (●) and $^2D$ (▲) states perturbed by $H_2$ at a pressure of 0.75 Torr. The calculated shift rates from Eq. (3) and broadening rates from Eq. (2a) are given by the solid lines.

## IV. DISCUSSION

### A. Low-energy electron-scattering resonances

It has been suggested by Matsuzawa[22] that measurements of shifts and broadenings in Rydberg states of alkali metals perturbed by molecular hydrogen would be a sensitive test for the presence of a proposed resonance[22] (with energy $E_r \sim 37$ meV and breadth $\Gamma_r \sim 3.7$ meV) in the low-energy electron scattering of $H_2$. Such a resonance would cause large oscillations with peak-to-peak amplitudes of $\sim 100$ MHz/Torr,[22] in the $n$ dependence of both broadening and shift cross sections. This is more than half of the observed shift rate for $H_2$ perturbers (Fig. 5). We observed no reproducible oscillations in the shift or broadening rates, implying either that the resonance in $e$-$H_2$ does not exist or has a width much larger than had been suggested (resulting in oscillations too small to be observed in our experiments).

### B. Asymptotic shifts and determination of scattering lengths

The theory for pressure shifts at high $n$ in Rydberg-atom–rare-gas systems is well established,[5–8] with the cross section $\sigma_\Delta$ given (in atomic units) by

$$\sigma_\Delta = \sigma_e + \sigma_p \ . \tag{1a}$$

Here, $\sigma_e$, the cross section for the Rydberg electron and perturber interaction, is

$$\sigma_e = \frac{2\pi L}{v} \tag{1b}$$

and $\sigma_p$, the cross section for the polarization attraction between perturber and Rydberg atom core, is

$$\sigma_p = -9.9\beta^2 \tag{1c}$$

with

$$\beta = \left[ \frac{\alpha}{2v} \right]^{1/3} .$$

$L$ and $\alpha$ are the perturber scattering length and polarizability, respectively, $v = \sqrt{8kT/(\pi\mu)}$ is the mean relative velocity of perturber and Rydberg atom, and $\mu$ is the reduced mass. Values of polarizability $\alpha$ are well known:[23] $2.663a_0^3$, $16.73a_0^3$, and $5.43a_0^3$ for Ne, Kr, and $H_2$. (For $H_2$ the isotropic part of the polarizability is used, since the anisotropy can be neglected.[22])

The asymptotic shift rates can be treated as measurements of the perturber scattering lengths $L$. Uncertainties in $\alpha$ and $T$ are insignificant in determining $L$, even for Ne where $\sigma_p$ is about one-half of the total. We find $L$ values of $(0.24\pm0.01)a_0$, $(-4.0\pm0.3)a_0$, and $(1.64\pm0.07)a_0$ for Ne, Kr, and $H_2$. In Table II these values are compared with results determined from other spectroscopic measurements of frequency shifts in Rydberg spectra. With the exception of the present values and those of Brillet and Gallagher,[4] all the results in Table II are from Doppler-broadened experiments at pressures $>1$ atm. In Table III the present values are compared with scattering lengths from other types of experiments, such as electron drift and swarm experiments. Our $L$ value for Ne is slightly smaller than those from other shift measurements; and while it agrees well with several of the results shown in Table III, it is somewhat larger than the values of Golovaniskii and Kabilan[24] and of Robertson,[26,27] which appear to be the most precise. For Kr, our result is significantly larger than other spectroscopic measurements, but agrees better with values from electron scattering. Our $H_2$ scattering length is much larger than results obtained by either method.

### C. Dependence of broadening and shift rates on principal quantum number $n$

The shift and broadening rates of Rydberg states have been calculated for rare-gas perturbers by combining a pseudopotential describing the electron-perturber interaction and a long-range potential for the ionic core-perturber attraction in the Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximation for the Rydberg electron wave functions.[7,8] This was first used by Omont[7] to derive an expression for the $n$ dependence of the broadening rate at high $n$. The method has also been used by Kaulakys[8] to include shift along with broadening, and extended to lower values of $n$. The predicted cross sections for broadening, $\sigma_\gamma$, and shift, $\sigma_\Delta$, are as follows:[8]

TABLE II. Scattering lengths (in units of $a_0$) determined from frequency shift measurements of Rb $^2S$ and $^2D$ Rydberg states perturbed by collisions with Ne, Kr, and $H_2$.

| Ne | Kr | $H_2$ | References |
|---|---|---|---|
| 0.24±0.01 | −4.0±0.3 | 1.64±0.07 | Present work |
| 0.24 | −3.2 | | Brillet and Gallagher (Ref. 4) |
| 0.27 | −1.9 | | Tan and Ch'en (Ref. 3) |
| 0.29 | | 1.39 | Ny and Ch'en (Ref. 3) |
| 0.29 | −2.7 | | Fuchtbauer *et al.* (Ref. 2) |
| | | 1.33 | Amaldi and Segré (Ref. 1) |

$$\sigma_\gamma = \begin{cases} 4\pi n^{*4}, & n^* < n_1^* \\ \dfrac{2\sqrt{\pi}\,|L|}{v} f(y), & n^* < 0.7 n_2^* \\ 5.5\beta^2 + \dfrac{2L^2}{v^2 n^{*4}} - \dfrac{1.7L^2\beta}{v^2 n^{*6}}, & n^* > n_2^* \end{cases} \tag{2a}$$

$$\sigma_\Delta = \begin{cases} 0, & n^* < 1.09 n_1^* \\ \dfrac{2\pi L}{v}\left[1 - \dfrac{n_1^{*8}}{n^{*8}}\right] - \dfrac{9.9\beta^3}{n^{*2}}\left[\dfrac{n^{*8}}{2n_1^{*8}} - 1\right], & 1.09 n^* < n^* < 0.73 n_2^* \\ \dfrac{2\pi L}{v}\left[1 - \dfrac{n_1^{*8}}{n^{*8}}\right] - 9.9\beta^2\left[1 - \dfrac{\beta}{n^{*2}}\right], & n^* > 0.73 n_2^* \end{cases} \tag{2b}$$

where

$$n_1^* = \left[\frac{|L|}{4v}\right]^{1/2}, \quad n_2^* = \left[\frac{|L|}{\alpha^{1/6} v^{5/6}}\right]^{1/3}, \quad y = \frac{4}{\pi}\left[\frac{n_1^*}{n^*}\right]^8,$$

$$f(y) = y^{-1/2}[1-(1-y)\exp(-y)] + y^{3/2}\mathrm{Ei}(-y),$$

TABLE III. Scattering lengths (in units of $a_0$) determined by electron scattering and swarm experiments.

| Ne | Kr | $H_2$ | References |
|---|---|---|---|
| 0.204±0.010 | −3.5±0.2 | | Golovanskii and Kabilan (Ref. 24) |
| 0.24 | | | Sol *et al.* (Ref. 25) |
| 0.214±0.005 | | | O'Malley and Crompton (Ref. 26) (reanalysis of Ref. 27) |
| 0.30 | | | Salop and Nakano (Ref. 28) |
| 0.20 | | | Hoffman and Skarsgard (Ref. 29) |
| | | 1.35±0.03 | Crompton *et al.* (Ref. 30) |
| | | 1.49 | Pack and Phelps (Ref. 31) |
| 0.39 | −3.2 | | O'Malley and Crompton (Ref. 26) (reanalysis of Ref. 32) |
| | | 1.40 | Wahlin (Ref. 33) |
| 0.24±0.02 | −3.7 | | O'Malley (Ref. 34) (reanalysis of Ref. 35) |

and Ei$(-y)$ is the exponential integral. Unlike his expression for $\sigma_\Upsilon$, Kaulakys's expression for $\sigma_\Delta$ is not averaged over a Maxwellian velocity distribution. When this is done, one obtains for $\sigma_e$ and $\sigma_p$ in Eq. (1a)

$$\sigma_e = \frac{2\pi L}{v}\left[\frac{2}{\sqrt{\pi}}(y_1)^{1/2}e^{-y_1}+(1-2y_1)\mathrm{erfc}(y_1)^{1/2}\right] \tag{3a}$$

$$\sigma_p = -9.9\beta^2\left[\frac{\beta}{n^{*2}}\left\{\left[\frac{3e^{-y_1}}{(\pi y_1)^{1/2}}+\left[\frac{3}{2y_1}-1\right]\mathrm{erfc}(y_1)^{1/2}\right]\right.\right.$$
$$\left.\left.-\frac{1}{y_1}\left[\frac{(y_2)^{1/2}}{\sqrt{\pi}}(2y_2+3)e^{-y_2}+\tfrac{3}{2}\mathrm{erfc}(y_2)^{1/2}\right]\right\}+\left[\frac{4}{\pi}\right]^{1/3}\Gamma(\tfrac{5}{3},y_2)\right], \tag{3b}$$

where

$$y_1 = 2y \quad \text{and} \quad y_2 = \frac{1}{2^{1.2}\pi}\left[\frac{n_2^*}{n^*}\right]^{7.2}$$

and $\Gamma$ is the incomplete gamma function.

We have used Eqs. (2a), (3a), and (3b) to calculate the broadening and shift rates for comparison with the present measured values. In these calculations the values used for the scattering lengths are those determined from the asymptotic shifts and are listed in Table II. In Fig. 2 the calculated shift rates for Kr and Ne perturbers are compared with measured rates. For Kr the observed increase in shift rates and approach to a constant value is well described by the theory. However, the steeper increase for the $^2S$ than that for the $^2D$ series at low $n^*$ values is not explained by the theory which provides for a dependence on $n^*$ only and not on the angular momentum $l$. For Ne the calculated and observed shift rates are in agreement, and the decreasing shifts as $n^*$ increases are explained by the dominance of the polarization (red) shift over the Fermi (blue) shift. Brillet and Gallagher[4] have reported a small increase in shift rate with $n$, for Rb $^2S$ states perturbed by Ne, but such a result cannot be explained by this theory.

In Fig. 3 the theoretical and measured broadening rates are compared for Kr and Ne perturbers. For Kr perturbers, both the magnitude and $n^*$ values for the maximum are in good agreement. The broadening is larger than predicted for higher $n^*$, probably due to the effects of inelastic collisions. Inelastic cross sections at large $n^*$ have been estimated by Omont:[7]

$$\sigma_{\mathrm{inel}} \sim \frac{4L^2}{n^* v} \tag{4}$$

for $(n^*)^2 \gg \Delta n^*/v$, where $\Delta n^*$ is the fractional part of the difference in effective quantum numbers for adjacent levels. For Kr the predicted broadening including this additional contribution is also shown in Fig. 3. Agreement with our results is significantly improved. For Ne the essentially coherent broadening rates agree with theory, and Eq. (4) gives a negligible contribution to broadening, due to the small scattering length. Finally, measurements of depopulation cross sections available for $n^* \sim 30-40$ have been included in the calculations and their effects are shown in Fig. 3. Measured inelastic cross sections[36] are larger for $^2S$ states than for $^2D$ states, reflecting the closeness of $n\,^2S$ and $(n-2)\,^2F$ states in Rb compared to the more isolated $^2D$ states. This should result in larger broadening rates for $^2S$ states perturbed by Kr, but there is no evidence of this in our observations. For Ne perturbers the effect of adding the inelastic rates is seen to be fairly small.

Finally, it is emphasized that no oscillations in frequency shifts or linewidths with $n$ were observed in the $^2S$ or $^2D$ spectra of Rb for collisions with Ne or Kr, in agreement with the results of Niemax and co-workers[15] for He, Ar, and Xe perturbers. This behavior differs from the oscillatory dependence with $n$ found for collisions of Rydberg alkali-metal atoms with ground-state alkali-metal atoms,[14,16] a result which remains unexplained.

For collisions with $H_2$, the broadening and shift rates calculated from Eqs. (2a), (3a), and (3b) do not agree with the measured dependence on $n^*$, as shown in Fig. 5. As $n^*$ increases, the observed shift rates gradually increase and broadening rates decrease. However, the calculated shift rates predict a small decrease, and the calculated broadening rates are $\sim 50\%$ smaller than observed rates. Such large discrepancies may be due to the use of a theory derived for atomic perturbers, which therefore does not include other degrees of freedom such as rotation. Rotation of $H_2$ could produce a sizable effect since the excitation energy for the ground state of $H_2$ (0.044 eV) corresponds to the binding energy of the Rb Rydberg electron for $n^* \sim 18$.

## V. CONCLUSIONS

Broadening and shift rates for rubidium $^2S$ and $^2D$ Rydberg states with $10 < n^* < 50$ have been measured for Ne, Kr, and $H_2$ perturbers. From the observed asymptotic shift rates at high $n^*$, we have derived perturber scattering lengths of $(0.24\pm0.01)a_0$ for Ne, $(-4.0\pm0.3)a_0$ for Kr, and $(1.64\pm0.07)a_0$ for $H_2$. The first two are in good agreement with other measurements, while the value for $H_2$ is significantly larger. The collision theory of Kaulakys[8] describes the observed dependence of shift and broadening rates on principal quantum number for Ne and Kr, but not for $H_2$. Also, there was no evidence of oscillations in the $H_2$ results, precluding the existence of a sharp resonance in low-energy electron scattering by $H_2$.

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