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# Collision broadening and shift of the potassium 4*P*-7*S* and 4*P*-5*D* lines by argon

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A two-step laser excitation technique has been used to investigate the collisional broadening and shift of excited-state potassium transitions. Values for the argon collisional broadening and shift constants for the potassium 4*p*-7*s* and 4*p*-5*d* transitions were determined from line shapes for argon pressures up to 100 Torr. The values of these constants (in units of $10^{-9}$ rad $s^{-1}$ $atom^{-1}$ $cm^3$) are
$(4P_{1/2} - 7S_{1/2})$: $\gamma = 11.60 \pm 0.07, \beta = -6.68 \pm 0.11$;
$(4P_{3/2} - 7S_{1/2})$: $\gamma = 11.49 \pm 0.15, \beta = -6.82 \pm 0.14$;
$(4P_{1/2} - 5D_{3/2})$: $\gamma = 8.64 \pm 0.07, \beta = -4.62 \pm 0.04$;
$(4P_{3/2} - 5D_{3/2})$: $\gamma = 8.58 \pm 0.10, \beta = -3.49 \pm 0.32$;
$(4P_{3/2} - 5D_{5/2})$: $\gamma = 9.13 \pm 0.10, \beta = -4.73 \pm 0.09$.
These broadening and shift constants are interpreted in terms of a Lennard-Jones interaction potential.

## I. INTRODUCTION

Measurements of the width and shift of spectral lines perturbed by collisions with neutral atoms can provide useful information about interactions involving excited atomic states. Previously, only a very limited number of excited-state transitions could be studied with thermal excitation sources since laboratory furnace temperatures are limited to a few thousand degrees, resulting in low atomic-state populations above ~ 1 eV.[1] In addition, conventional absorption and emission methods resulted in large statistical errors. These limitations can be overcome through the use of tunable dye lasers which offer a number of advantages: (1) The wide tunability of dye lasers and the availability of multiphoton and multistep excitation techniques permits the study of virtually any excited-state atomic transition, (2) the high spectral irradiance of lasers allows us to significantly populate atomic energy levels several eV above the ground state and to make measurements at low atom concentrations using fluorescence detection techniques, (3) the small instrumental width (linewidth) possible with laser sources permits increased measurement resolution (Doppler limited), and (4) nonlinear spectroscopic techniques are available to remove the presence of Doppler broadening thereby permitting collisional broadening and shift measurements to be made for one- and two-photon transitions at perturber pressures below 1 Torr.[2-6]

In this paper we report measurements of the argon collisional broadening and shift of the potassium 4*p*–7*s* and 4*p*–5*d* transitions using a two-step laser excitation technique. Measurements were made for perturber pressures in the range 0 to 100 Torr. The resulting line shapes were analyzed within the approximations of the impact theory of collisional broadening taking into account the line asymmetry which was observed at the higher perturber pressures. This analysis yielded the collisional broadening and shift parameters for the potassium 4*p*–7*s* and 4*p*–5*d* transitions.

## II. EXPERIMENTAL DETAILS

The direct population of the potassium intermediate 4*p* level with a multimode dye laser resulted in complex 4*p*–7*s* and 4*p*–5*d* line shapes which reflected the ground-state velocity groups promoted to the 4*p* level by the multimode laser. At zero perturber gas pressure this arrangement resulted in the complex line shape shown in Fig. 1(a). Such line shapes are difficult to analyze. For ease of analysis, a Doppler-broadened velocity distribution in the intermediate 4*p* level is desirable.

We were able to produce a Doppler-broadened velocity distribution in an intermediate 4*p* level (e.g., $4^2P_{3/2}$) by directly exciting the other 4*p* level level ($4^2P_{1/2}$) and relying on collisions to populate the intermediate 4*p* level ($4^2P_{3/2}$). At a temperature of ~ 110°C the gas-phase potassium number density of ~ $9 \times 10^{11}$ $cm^{-3}$ resulted in a K-K collision rate sufficiently high to produce a symmetric Doppler-broadened line shape for the excited-state transition ($4^2P_{3/2} \rightarrow 7^2S_{1/2}$). This is shown in Fig. 1(b).

The experimental apparatus for our neutral particle collisional broadening and shift measurements of potassium excited-state transitions is show in Fig. 2. The red output from a krypton-ion laser is used to pump an Oxazine-1 cw dye laser (Spectra-Physics, model 375). At a pump power level of 4 W, about 0.5 W of dye laser power is available at 766.5–769.9 nm in a bandwidth of ~ 0.04 nm. The unfocused laser beam was split into two nearly equal-intensity beams and directed down the axes of two quartz vapor cells containing potassium. These vapor cells are contained in

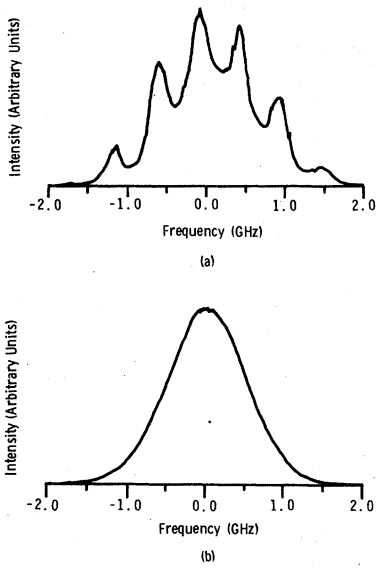


FIG. 1. (a) $4\,^2P_{1/2}$-$7\,^2S_{1/2}$ line shape with multimode laser excitation of the $4\,^2P_{1/2}$ level. (b) $4\,^2P_{1/2}$-$7\,^2S_{1/2}$ line shape with multimode laser excitation of the $4\,^2P_{3/2}$ level and collisional population of the $4\,^2P_{1/2}$ level.

two-stage temperature-controlled ovens with the lower oven maintained at a temperature of ~110° C. The first of these two cells (reference) contained potassium with no perturber gas present and served as a reference for the line-shift measurement. The second cell contained potassium and a variable pressure of argon (99.999%) which was controlled by a vacuum- and gas-handling system. A capacitance manometer (MKS Baratron, model 222; 0–100-Torr range, and 2% of reading accuracy) was used to measure the pressure of the argon admitted to the closed measurement cell.

The Oxazine-1 dye laser was tuned to excite either the $4\,^2S_{1/2} \rightarrow 4\,^2P_{1/2}$ or $4\,^2S_{1/2} \rightarrow 4\,^2P_{3/2}$ transitions at 769.9 and 766.5 nm, respectively, by monitoring the resonance fluorescence with a photomultiplier tube (RCA C31034) and picoammeter (not shown in Fig. 2). Long-term drifts in the laser wavelength due to changes in the ambient temperature made it necessary to periodically retune the laser during the course of these measurements.

The green output from an argon-ion laser was used to pump the Rhodamine 6G (R6G) cw dye laser (Coherent, Inc., model 599-21) which was used to measure the $4p$-$7s$ and $4p$-$5d$ transition line shapes. This laser is frequency stabilized with a linewidth of <5 MHz and can be continuously scanned over a wavelength interval of 1 $cm^{-1}$. The unfocused output (30-50 mW) from this laser is split into two equal beams and directed through the potassium vapor cells in a direction opposite that of the Oxazine-1 dye laser beams. The two beams overlap in the center of the vapor cells, crossing at a small angle (~20 mrad). After traversing the measurement cell, the R6G dye laser beam is redirected through the reference cell to saturate the excited-state transition. The very narrow Lamb dip produced in this manner is used to accurately locate the transition line center for the line-shift measurements.

The potassium excited-state line shapes were measured by scanning the R6G dye laser and detecting the fluorescence emission from the $5p$ level. This fluorescence was detected through an interference filter (404.7 nm, 10 nm full width half-maximum bandwidth) with a photomultiplier tube (RCA 8850). The R6G dye laser beams were modulated with mechanical light choppers and the fluorescence signals processed by means of lock-in amplifiers (Princeton Applied Research, model HR-8).

A 50-cm confocal Fabry-Perot etalon (Burleigh Instruments, model CF-500) in a temperature-stabilized oven provided the frequency calibration for the broadening and shift measurements. The free-spectral-range of this etalon was measured to be 150.7±0.1 MHz with the calibration technique of Goldsmith *et al.*[7]

As the R6G dye laser was scanned across the potassium excited-state transitions, the fluorescence signals from the reference and measurement cells and the etalon reference markers were recorded on two synchronously driven dual-pen strip chart recorders. The resultant curves were digitized, normalized, and scaled in frequency using a programmable calculator-digitizer system (Hewlett-Packard, model 9100B programmable calculator with model 9107A digitizer). The digit-

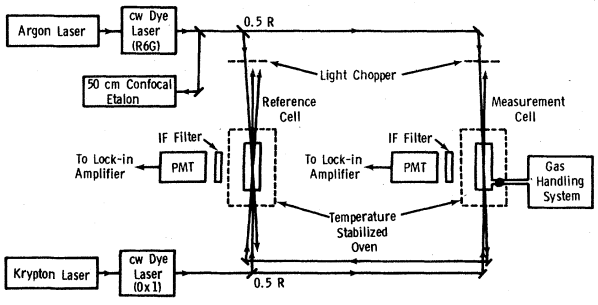


FIG. 2. Experimental apparatus for collisional-broadening and shift studies of potassium excited-state transitions.

ized data were then analyzed on a CDC 6600 computer to determine the collisional broadening and shift parameters.

## III. PROFILE ANALYSIS

The broadening and shift of the potassium $4p$-$7s$ and $4p$-$5d$ transitions were measured at various pressures of argon in the range 0 to 100 Torr. In the analysis of the experimental data we made the usual assumption that the collision and Doppler-broadening mechanisms were strictly independent. For each set of measurements corresponding to a particular transition, the Doppler width was determined from a least-squares fit of a Gaussian line profile fit to the data recorded at zero perturber gas pressure. The collisional broadening and shift parameters at each argon pressure were then determined by fitting the experimental data to a Voigt profile with a least-squares fitting routine. To reduce the analysis time and expense in performing the least-squares fit, our computer code approximated the Voigt profile with a routine developed by Pierluissi *et al.*[8] This routine uses a three-region approximation to the Voigt profile and has a reported rms deviation of less than 1 part in $10^4$.

At the higher perturber gas pressures, the argon-broadened line profiles were found to be asymmetric, with the red wing being slightly broader than the violet wing by an amount which increased with pressure. This asymmetry is shown in Fig. 3(a) for the $4\,^2P_{1/2} \rightarrow 7\,^2S_{1/2}$ transition at 100-Torr argon. The presence of asymmetric line broadening is indicative of a breakdown in the impact approximation which generally assumes that the duration of each collision is negligible and therefore neglects radiation during collisions. Although of a somewhat smaller magnitude, similar asymmetric line shapes have been reported in collisional-broadening measurements of the calcium and cesium resonance lines.[9-10] More general theories of pressure broadening which include additional terms to account for radiation during collisions have predicted asymmetric line shapes.[11,12] In our Voigt fitting routine, we added an additional term linear in the frequency offset $\nu - \nu_0$ from line center ($\nu_0$) to account for the line-shape asymmetry. Although this term should strictly be inside the Voigt integral, we expect the difference between our approximation and the exact solution to be minor as evidenced by the good fits to the experimental data [see Fig. 3(b)]. In the case of the $4\,^2P_{3/2} \rightarrow 5\,^2D_{5/2}$ transition the data were poorly fitted at pressures above about 10 Torr due to the overlapping wings of the stronger $4\,^2P_{3/2} \rightarrow 5\,^2D_{5/2}$ transition located about 0.5 $cm^{-1}$ to the red. Thus for the $4\,^2P_{3/2} \rightarrow 5\,^2D_{3/2}$ transition only the data for pressures up to 10 Torr were used in determining the collisional-broadening and shift constants.

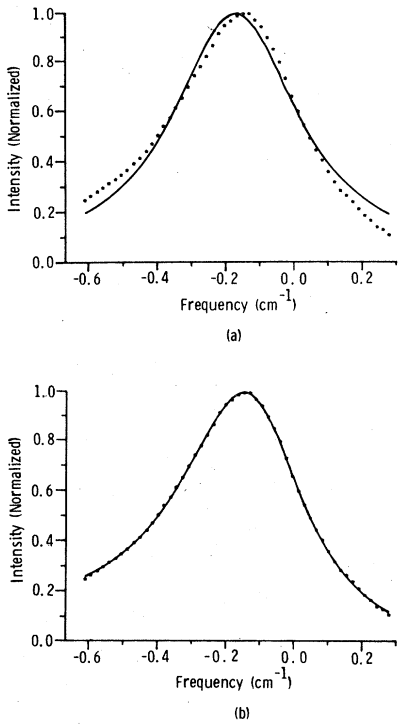


FIG. 3. $4\,^2P_{1/2}$-$7\,^2S_{1/2}$ line broadened by 100-Torr argon. (a) * Experimental data—Voigt fit to experimental data. (b) * Experimental data—Voigt fit to experimental data with line-shape asymmetry correction.

## IV. RESULTS AND DISCUSSION

The Lorentzian half-halfwidth $\gamma$ and shift $\beta$ calculated for each argon pressure were fitted as a function of the argon pressure using a linear least-

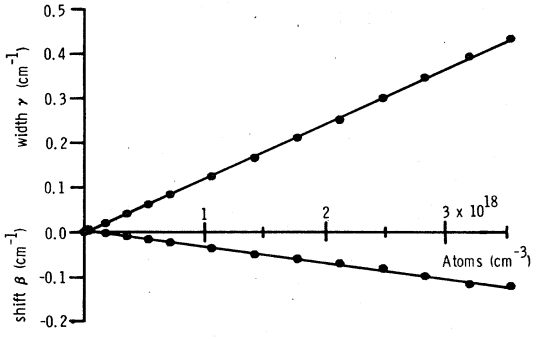


FIG. 4. Width $\gamma$ (half-width at half-maximum) and shift $\beta$ of the potassium $4\,^2P_{1/2}$-$7\,^2S_{1/2}$ transition with argon. The straight lines represent a linear least-squares fit to the data.

TABLE I. Argon collisional broadening and shift of potassium.[a]

| Transition | Broadening $\gamma$ (half width at half maximum) ($10^{-9}$ rad s$^{-1}$ atom$^{-1}$ cm$^3$) | Shift $\beta$ ($10^{-9}$ rad s$^{-1}$ atom$^{-1}$ cm$^3$) | $\beta/2\gamma$ |
|---|---|---|---|
| $4\,^2P_{1/2} \rightarrow 7\,^2S_{1/2}$ | 11.60 ± 0.07 | −6.68 ± 0.11 | −0.29 |
| $4\,^2P_{3/2} \rightarrow 7\,^2S_{1/2}$ | 11.49 ± 0.15 | −6.82 ± 0.14 | −0.30 |
| $4\,^2P_{1/2} \rightarrow 5\,^2D_{3/2}$ | 8.64 ± 0.07 | −4.62 ± 0.04 | −0.27 |
| $4\,^2P_{3/2} \rightarrow 5\,^2D_{3/2}$ | 8.58 ± 0.10 | −3.49 ± 0.32 | −0.20 |
| $4\,^2P_{3/2} \rightarrow 5\,^2D_{5/2}$ | 9.13 ± 0.10 | −4.73 ± 0.09 | −0.26 |

[a] Negative shifts are towards the red.

squares fitting routine. A representative curve for the $4\,^2P_{1/2} \rightarrow 7\,^2S_{1/2}$ transition is shown in Fig. 4. There is a linear variation of both width and shift with perturber number density over the whole of the pressure range investigated. This linear variation is characteristic of the impact-broadening region where binary interactions predominate. The pressure broadening contributes a Lorentzian profile of total half-intensity width $2\gamma$ shifted by an amount $\beta$ with respect to the unperturbed line. The observed shift of the lines to longer wavelengths (negative $\beta$) with increasing perturber pressure is indicative of an attractive long-range potential in the upper level.

The calculated variations of $\gamma$ and $\beta$ with perturber number density are shown in Table I for all the transitions measured. The broadening and shift parameters measured for the $4p$-$7s$ and $4p$-$5d$ transitions are much larger than those reported for the $4s$-$4p$ and $4s$-$5p$ lines[13,14] owing to the larger spatial extension of the excited-state wave functions. Similarly, the broadening and shift for the $4p$-$7s$ lines are larger than those for the $4p$-$5d$ lines.

The ratios of the shift to full width at half-maximum ($\beta/2\gamma$) are also presented in Table I for each transition. The calculated ratios lie in the range -0.20 to -0.30 which is significantly smaller than the theoretical ratio of -0.363 for a pure van der Waals ($r^{-6}$) interaction.[15] Thus it follows that the long-range van der Waals interaction, although dominant, is not adequate for our measurements. It is therefore useful to examine a Lennard-Jones difference potential of the form $C_{12}r^{-12}-C_6r^{-6}$ which can independently fit the shift to width ratio. The $C_6$ and $C_{12}$ coefficients can be calculated from the measured broadening and shift parameters using the analysis of Hindmarsh *et al.*[16] These experimentally determined $C_6$ and $C_{12}$ coefficients are presented in Table II. In addition, we have listed in Table II theoretical values for $C_6$ calculated using the expression[15]:

$$C_6 = e^2\sigma(\langle r_f^2\rangle - \langle r_i^2\rangle).$$

In this expression, $e$ is the electronic charge, $\sigma$ the polarizability of the argon perturber gas, and $\langle r_f^2\rangle$ and $\langle r_i^2\rangle$ the quantum-mechanical average values of $r^2$ for the upper and lower states of the transition, respectively. For $\langle r^2\rangle$ we have used the expression[15]

$$\langle r^2\rangle = \tfrac{1}{2}a^2(n^*)^2[5(n^*)^2 + 1 - 3\ell(\ell+1)],$$

where $a_0$ is the Bohr radius, $n^*$ the effective quantum number, and $\ell$ the orbital quantum number. The values of $C_6$ were calculated using Kuhn's values[17] of $n^*$ and Dalgarno and Kingston's value[18] for $\sigma$. In Table II the experimentally determined values for $C_6$ are about 2.5 times the theoretical values for the $4p$-$7s$ transitions while there is good agreement between the experimental and theoretical values for the $4p$-$5d$ transitions.

## V. CONCLUSION

We have utilized a two-step laser excitation technique to accurately measure the argon collisional-broadening and shift constants of excited-state potassium transitions. Our measurements were fit to a Lennard-Jones difference potential to obtain a better characterization of the interactions.

TABLE II. $C_6$, $C_{12}$ for potassium-argon interactions.

| Transition | $C_6$ expt (erg cm$^6$) | $C_{12}$ expt (erg cm$^{12}$) | $C_6$ theory (erg cm$^6$) |
|---|---|---|---|
| $4\,^2P_{1/2} \rightarrow 7\,^2S_{1/2}$ | $3.5\times10^{-56}$ | $9.2\times10^{-96}$ | $1.4\times10^{-56}$ |
| $4\,^2P_{3/2} \rightarrow 7\,^2S_{1/2}$ | $3.6\times10^{-56}$ | $7.2\times10^{-96}$ | |
| $4\,^2P_{1/2} \rightarrow 5\,^2D_{3/2}$ | $1.5\times10^{-56}$ | $2.4\times10^{-96}$ | |
| $4\,^2P_{3/2} \rightarrow 5\,^2D_{3/2}$ | $7.1\times10^{-57}$ | $5.4\times10^{-96}$ | $1.1\times10^{-56}$ |
| $4\,^2P_{3/2} \rightarrow 5\,^2D_{5/2}$ | $1.6\times10^{-56}$ | $3.7\times10^{-96}$ | |

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