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Study of velocity-changing collisions in excited Kr using saturation spectroscopy

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A saturated-absorption experiment is used to measure the effects of velocity-changing collisions between Kr* metastable atoms $(4p^5 5s[3/2]_2)$ and He and Ar perturbers. Comparison between experimental profiles and profiles calculated assuming hard-sphere collisions between Kr* and perturber atoms confirms the calculations of Borenstein and Lamb concerning the change of velocity associated with a collision. Furthermore it is found that the rate of velocity-changing collisions is consistent with the predictions of kinetic theory.

I. INTRODUCTION

We report the first systematic saturation spectroscopy study of velocity-changing collisions (VCC) between electronically excited active atoms and ground-state perturbers. By choosing a perturber–active-atom mass ratio less than unity, we are able to clearly isolate the effects of close-encounter collisions. As such, our analysis represents an initial step in obtaining specific information on the short-range part of excited-state interatomic potentials by monitoring VCC using saturation spectroscopy, and it indicates the potential of this method for studying scattering in short-lived excited states.

The study of velocity-changing collisions (VCC) in the ground and excited states of atoms or molecules using laser spectroscopic techniques has received increased attention over the past few years.[1-9] In a typical experiment one uses a narrow-band laser source of frequency Ω tuned near an atomic-transition frequency ω to selectively excite atoms with an axial velocity $v_z = (\Omega-\omega)/k$, $(k=\Omega/c)$; only atoms with this axial velocity will see a Doppler-shifted laser frequency in resonance with their own transition frequency. A probe laser beam is then used to monitor any velocity change undergone by these excited atoms. Although only one velocity component is studied by this technique, information on the nature of the collision interaction can be inferred from the results of such experiments. Theoretical aspects of the problem are examined in Refs. 10 – 12.

To date, experiments have been analyzed assuming collisions are of a "weak" or "strong" nature. Weak collisions involve relatively small velocity changes Δu ($\Delta u \ll u$ = width of the equilibrium velocity distribution) and presumably characterize collisions with large impact parameters. A strong collision usually refers to a collision which, on average, completely thermalizes the atom's velocity distribution $(\Delta u \approx u)$ as might occur following a close collision between a heavy perturber and a light active atom. In a previous publication, we reported on the influence of collisions on saturated absorption profiles of the 557-nm line of Kr I [8]; Kr*-Kr and Kr*-Xe collisions were considered and interpreted in terms of a strong-collision model.

In this work, we study the effect of close-encounter collisions between Kr* atoms and He or Ar perturbers, for which both the strong-and weak-collision models are inadequate. Saturated-

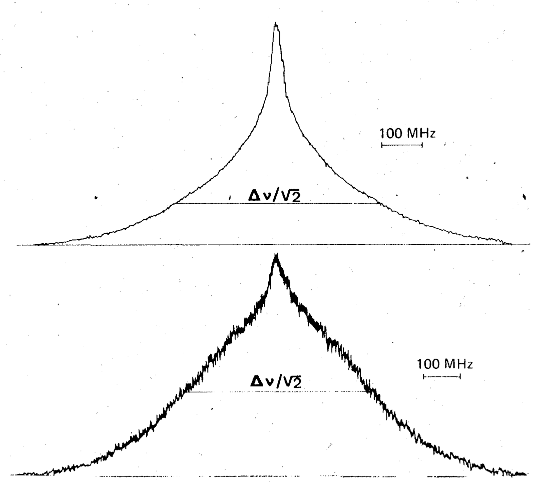

FIG. 1. Typical recording of the 557-nm line of Kr I in the presence of He and Ar perturbers. Upper trace: P_{Kr}, 8 mTorr; P_{He}, 260 mTorr. Lower trace: P_{Kr}, 8 mTorr; P_{Ar}, 220 mTorr. The horizontal line represents the Doppler width $/\sqrt{2}$. In this experiment the frequency scale is determined by Fabry-Perot fringes spaced by 83 MHz.

absorption line shapes for the 557-nm transition ($4p^55s[\frac{3}{2}]_2 - 4p^55p'[\frac{1}{2}]_1$) in Kr I were obtained using an experimental arrangement that has been described elsewhere.[8] The pressure of krypton was kept at a fixed value of 8 mTorr and the pressures of He and Ar perturbers were varied between 0 and 700 and 0 and 250 mTorr, respectively. Typical recordings of saturated-absorption profiles are shown on Fig. 1. Saturated-absorption profiles have shapes and widths varying with mass and pressure of perturbers; they could be consistently fit over the entire pressure ranges assuming they are the sum of a narrow resonance of width 2γ [full width at half maximum (FWHM)] and a broad background. The narrow component corresponds to atoms that have not undergone VCC, and the broad one corresponds to atoms that have experienced VCC. The shape of the background signals provides direct information characterizing the strength and cross-section for Kr*-Kr, Kr*-He, and Kr*-Ar collisions. In this paper we use a hard-sphere model to describe the collisions, but more detailed models could be used in the future.

II. THEORETICAL ASPECTS

The following assumptions, consistent with the experimental results, were used to arrive at a theoretical line shape.

(i) The narrow resonance in the line shape, as modified by phase-interrupting collisions, saturation broadening, weak VCC,[6,7,9-13] beam misalignment, and laser jitter can still be well approximated by a Lorentzian with some appropriate width 2γ.

(ii) The VCC redistribute the velocity of Kr* in the $4p^55s[\frac{3}{2}]_2$ metastable state; effects of VCC on the rapidly decaying $4p^55p'[\frac{1}{2}]_1$ state can be neglected.

(iii) Close-encounter Kr*-He or Kr*-Ar collisions can be characterized as hard-sphere collisions with a collision kernel of the Keilson-Storer type[14]

$$W(\vec{v}'\to\vec{v}) = \Gamma_2[\pi(\Delta u)^2]^{-3/2} \times \exp[-(\vec{v}-\alpha\vec{v}')^2/(\Delta u)^2], \quad (1)$$

where $W(\vec{v}'\to\vec{v})$ is the probability density per unit time to have a velocity change from $\vec{v}'$ to $\vec{v}$,

$$\Delta u = (1-\alpha^2)^{1/2} u \quad (2)$$

is $\sqrt{2}$ times the rms velocity change per collision, u is the most probable speed of the equilibrium distribution, α is a parameter related to the strength of a collision, and Γ_2 is the rate of VCC. For hard-sphere collisions, Borenstein and Lamb[15] have calculated α as a function of perturber-active-atom mass ratio using a computer simulation of the collisions.

(iv) A single VCC is sufficient to remove atoms from the velocity holes created by the field, i.e., $\Delta u > 2\gamma/k$. This condition is satisfied in our experiment.

(v) The Kr*-Kr collisions can be approximated as "strong" collisions leading to a thermal distribution after a single average collision. Hard-sphere collisions between equal-mass atoms or excitation-exchange collisions are approximately described by such a collision model.[15] The data of Fig. 1 contain both the Kr*-Kr and Kr*-He or Ar contributions to the broad background.

Assuming that the field strengths are weak enough to justify a rate-equation approximation to the atom-field interaction and using the above collision model, one arrives at the saturated-absorption line shape[10-12] for equal pump and probe frequencies,

$$I(\Delta) \propto \left[\frac{1}{2}\frac{\gamma^2}{\gamma^2+\Delta^2} + \sqrt{\pi}\frac{\gamma}{ku}\frac{\Gamma^t\Gamma_1}{\Gamma_0(\Gamma_0+\Gamma_1)}\exp\left(\frac{-\Delta^2}{k^2u^2}\right) + \sqrt{\pi}\frac{\gamma}{ku}\sum_{n=1}^{\infty}\left(\frac{\Gamma_2}{\Gamma^t}\right)^n \frac{1}{(1-\alpha^{2n})^{1/2}}\exp\left(\frac{-\Delta^2}{k^2u^2}\frac{1+\alpha^n}{1-\alpha^n}\right)\right]\exp\left(\frac{-\Delta^2}{k^2u^2}\right), \quad (3)$$

where $\Delta = \Omega - \omega$ is the detuning, Γ_1 is the Kr*-Kr VCC rate, Γ_2 is the Kr*-He or Kr*-Ar VCC rate,

$$\Gamma_0 = \tau^{-1},$$

where τ is the lifetime of Kr* atoms in the laser beams (experimentally, since the natural lifetime of the metastable is very long, τ is determined by the transit time in the beams, which will be pressure dependent) and

$$\Gamma^t = \Gamma_0 + \Gamma_1 + \Gamma_2 .$$

The line shape (3) has a simple interpretation. The first term arises from atoms undergoing no VCC during the time τ, the second term arises from atoms undergoing at least one Kr*-Kr collision in the time τ leading to a complete thermalization and the final term corresponds to atoms undergoing no Kr*-Kr collisions and some Kr*-He or Kr*-Ar collisions in the time τ leading to a partial thermalization of the sample.

III. ANALYSIS OF THE DATA

Experimental profiles were compared to theoretical line shapes corresponding to expression (3) by making the following assumptions: For the fixed Kr pressure of 8 mTorr chosen in this experiment we have taken the rate Γ_1 for thermalizing Kr*-Kr collisions as $\Gamma_1 = 1.4\times 10^5$/sec determined from our previous experiment.[8] We have used a hard-sphere model for the determination of α and Γ_2; α was chosen from the results of Borenstein and Lamb[15]: $\alpha = 0.936$ for Kr*-He and $\alpha = 0.6$ for Kr*-Ar. {A larger value of α implies a smaller Δu [cf. Eq. (2)]; for perturber–active atom mass ratios $\gg 1$, $\alpha \approx 0$, and for perturber–active-atom mass ratios $\ll 1$, $\alpha \approx 1$.} The rate Γ_2 was chosen from the kinetic theory of gases with the "radii" of atoms as indicated by Allen,[16] $\Gamma_2 = 1.0\times 10^4 p$ sec^{-1} for Kr*-He and $\Gamma_2 = 0.53\times 10^4 p$ sec^{-1} for Kr*-Ar, where p is the perturber pressure in mTorr. At each perturber pressure, the values of the two parameters γ and Γ_0 were varied so as to minimize the rms error of the fit of Eq. (3) to the data. Typical examples for He and Ar are shown on Fig. 2. For the entire pressure range studied the data could be fit very well (i.e. with a normalized rms error ≤ 0.05) by Eq. (3).

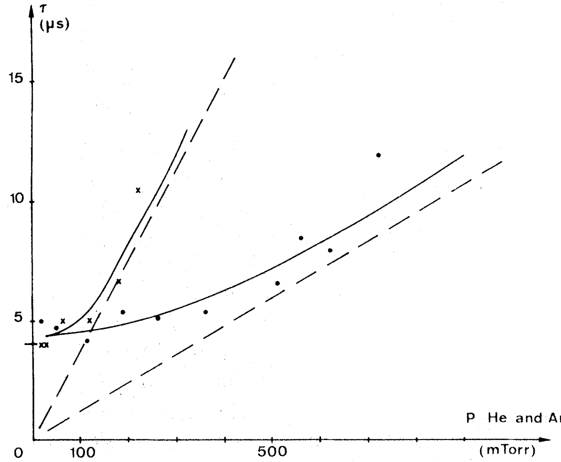

FIG. 3. Variations of the transit time τ vs perturber pressures. (Dots correspond to He-Kr* and crosses to Ar-Kr* data.) The broken lines correspond to the variations given by the classical law of diffusion.

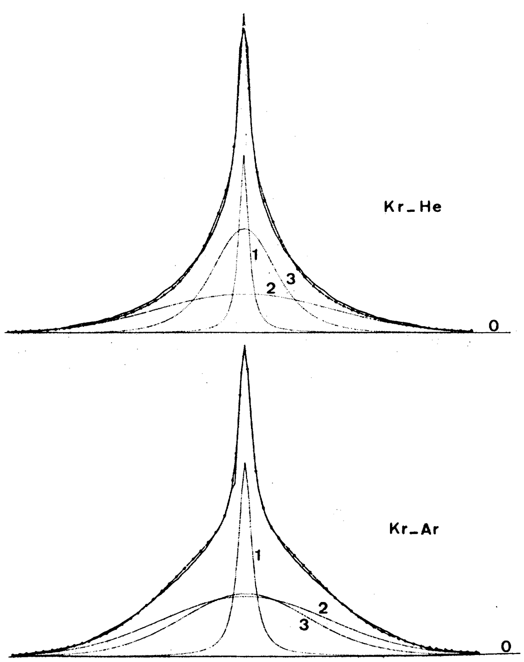

FIG. 2. Typical fits for He and Ar perturbers. Upper trace: P_{Kr}, 8 mTorr; P_{He}, 110 mTorr. Lower trace: P_{Kr}, 8 mTorr; P_{Ar}, 120 mTorr. The solid line corresponds to the recorded profile and large dots represent the calculated profiles corresponding to the best fit. The three dotted lines represent the contributions from the three terms of Eq. (3): Curve 1 corresponds to the narrow resonance (first term), curve 2 corresponds to the Gaussian background (second term) arising from Kr*-Kr collisions, and curve 3 corresponds to the contribution of VCC (third term) arising from Kr*-He and Kr*-Ar collisions.

The values of $\tau = \Gamma_0^{-1}$ obtained for the various perturber pressures are plotted on Fig. 3. There is an increase of τ with pressure similar to the one observed for Kr*-Kr collisions[8]; accordingly, we conclude that τ is determined by the transit times of atoms in the beams. The findings are consistent with the premise that heavier perturbers are more effective in increasing the transit time than lighter ones. The two curves converge to the same transit time at low pressure ($\tau_0 \approx 4$ μs) in accordance with the value measured in pure Kr at 8 mTorr; for the highest pressures they tend roughly to the linear variations given by the classical law of diffusion.[8]

The FWHM of the VCC contributions (third term in Eq. 3) as a function of perturber pressures is shown on Fig. 4. As may be seen, both widths approach the thermal-equilibrium value $\Delta\nu/\sqrt{2} = 510$ MHz as the perturber pressure is increased. The heavier Ar atoms produce thermalization at a lower pressure than the lighter He ones (see also Fig. 1) consistent with the hard-sphere collision model. A value for these widths obtained at very low pressure can be deduced from Eq. (3) by taking the $n=1$ term in the sum. These values are indicated in Fig. 4 by short-dashed lines.

We have tried various values of α around the values mentioned above, $\alpha = 0.93$ for Kr*-He and $\alpha = 0.6$ for Kr*-Ar. If α is chosen too small the

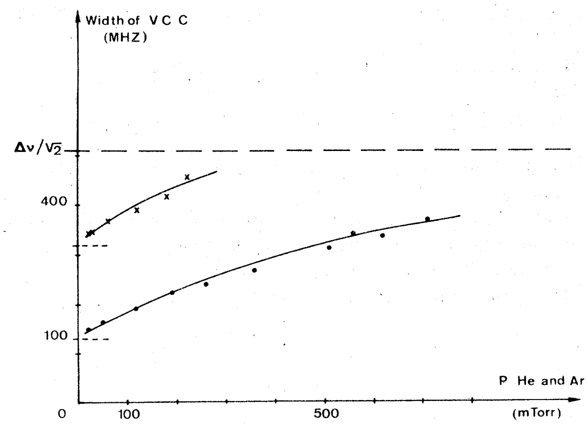

FIG. 4. Variations of the width of the VCC contributions [third term in Eq. (3) of text] vs perturber pressure (dots correspond to He and crosses to Ar perturbers). The horizontal dashed line corresponds to the thermal-equilibrium limit. The short horizontal dashed lines correspond to the width of the $n=1$ contribution in Eq. (3).

resulting Δu is too large to fit the data (for example, $\alpha=0.85$ for He is a lower limit); on the other hand if α is chosen too large, the data could be fit only with unacceptably small values for 2γ (for He, $\alpha=0.98$ is an upper limit). We conclude that

$$\alpha=0.93\pm0.03 \text{ for Kr*-He,}$$

$$\alpha=0.6\pm0.2 \text{ for Kr*-Ar,}$$

where the error limits are obtained by those values of α leading to a normalized rms error of 0.2 in the fitting procedure.

The values of Γ_2 that we have chosen have been calculated using the ground-state kinetic-theory radii tabulated by Allen.[16] Values of Γ_2 determined in the same manner but by choosing for Kr* metastables a radius corresponding to the excited electron[17] have also been tried. Results are less consistent; first, the transit time takes on a nearly constant value ($\approx 3\ \mu$s) over the range of pressure and, second, the width of the narrow resonance is too small. Additional experiments with various perturber–active-atom mass ratios may help to clarify the manner in which the effective excited-state radius should be chosen.

We have tried also to fit the profiles by leaving free the three parameters γ, Γ_0, and Γ_2. For He the variations of Γ_2 with pressure showed, as expected, a linear increase at low pressure, but a decrease at high pressure ($p>200$ mTorr). This deviation from the linear increase was attributed to the fitting procedure used since at high pressures VCC contribute well into the wings of the thermal distribution and it is difficult to distinguish between Kr*-Kr and Kr*-He contributions. The low-pressure regime gave $\Gamma_2=0.95\times10^4 p$ sec^{-1} confirming our choice for Γ_2 determined from kinetic theory and Allen's values.

IV. CONCLUSION

We have arrived at a consistent picture of VCC in the metastable $4p^5 5s[\frac{3}{2}]_2$ state of krypton caused by argon and helium perturbers, based on a hard-sphere collision model. Future experiments of this type in two- or three-level systems may be expected to provide a more sensitive probe of the short-range collisional interaction, while providing a new method for studying excited-state scattering.

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[1]T. W. Hänsch and P. E. Toschek, IEEE J. Quantum Electron. 5, 61 (1969); P. W. Smith and T. W. Hänsch, Phys. Rev. Lett. 26, 740 (1971); R. Keil, A. Schabert, and P. Toschek, Z. Phys. 261, 71 (1973); I. M. Beterov, Y. A. Matyugin, and V. P. Chebotaev, Zh. Eksp. Teor. Fiz. 64, 1495 (1973) [Sov. Phys.-JETP 37, 756 (1973)]; T. W. Meyer and C. K. Rhodes, Phys. Rev. Lett. 32, 637 (1974); R. G. Brewer, R. L. Shoemaker, and S. Stenholm, *ibid.* 33, 63 (1974); R. L. Shoemaker, S. Stenholm, and R. G. Brewer, Phys. Rev. A 10, 2037 (1974); J. Schmidt, P. R. Berman, and R. G. Brewer, Phys. Rev. Lett. 31, 1103 (1973); P. R. Berman, J. M. Levy, and R. G. Brewer, Phys. Rev A 11, 1668 (1975).

[2]T. Kan and G. J. Wolga, IEEE J. Quantum Electron. 7, 141 (1971).

[3]J. Brochard and Ph. Cahuzac, J. Phys. B 9, 2027 (1976).

[4]Ph. Cahuzac, O. Robaux, and R. Vetter, J. Phys. B 9, 3165 (1976).

[5]W. K. Bischel and C. K. Rhodes, Phys. Rev. A 14, 176 (1976).

[6]A. T. Mattick, N. A. Kurnit, and A. Javan, Chem. Phys. Lett. 38, 176 (1976).

[7]L. S. Vasilenko, V. P. Kochanov, and V. P. Chebotaev, Optics Commun. 20, 409 (1977).
[8]C. Brechignac, R. Vetter, and P. R. Berman, J. Phys. B 10, 3443 (1977).
[9]Ph. Cahuzac, E. Marie, O. Robaux, R. Vetter, and P. R. Berman, J. Phys. (to be published).
[10]A. P. Kolchenko, A. A. Pukhov, S. G. Rautian, and A. M. Shalagin, Zh. Eksp. Teor. Fiz. 62, 2097 (1972) [Sov. Phys. JETP 36, 619 (1973)].
[11]P. R. Berman, Phys. Rev. A 13, 2191 (1976).
[12]P. R. Berman, Adv. At. Mol. Phys. 13, 57 (1978).
[13]V. A. Alexseev, T. L. Andreeva, and I. I. Sobelman, Zh. Eksp. Teor. Fiz. 64, 813 (1973) [Sov. Phys.- JETP 37, 413 (1973)].
[14]J. Keilson and J. E. Storer, Q. Appl. Math. 10, 243 (1952).
[15]M. Borenstein and W. E. Lamb, Phys. Rev. A 5, 1311 (1972).
[16]C. W. Allen, *Astrophysical Quantities*, 2nd ed. (University of London, London, 1963), p. 45. These radii are approximately gas kinetic radii of monoatomic molecules and correspond to the distance of closest approach in the formation of molecules.
[17]M. Aymar (private communication).