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Measurement of a metastability-exchange cross section in krypton

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The metastability-exchange cross section between $(^3P_2)$Kr atoms and $(^1S_0)$Kr atoms is measured by means of a two-laser saturated-absorption experiment performed on the $\lambda = 557$-nm transition. A study of velocity changes occurring in pure ^{86}Kr and in (^{86}Kr–^{78}Kr) discharges leads to a value for the cross section $Q = (75 \pm 10)$ Å^2.

I. INTRODUCTION

Saturated-absorption techniques have been used in a number of experiments to study the velocity changes that result from collisions between active atoms and ground-state perturbers. These velocity changes alter the narrow saturated-absorption profiles in basically two ways:

Velocity changes that drive the active atoms out of the hole (homogeneous profile) which is burned in the velocity distribution by the pump field give rise to a broad background superimposed on the narrow resonance.[1-7]

Small velocity changes that occur at large impact parameters tend to confine the active atoms within the homogeneous profile. The resultant broadening of the narrow resonance is, in general, a nonlinear function of pressure.[8-13]

As for the first effect, it was extensively studied in experiments performed on the line of Kr I at $\lambda = 557$ nm (Refs. 5–7). It was shown, in particular in Ref. 5 that even at low pressures and low saturation there exists a large Gaussian background whose width is the Doppler one and whose origin is associated with Kr*-Kr collisions. Its magnitude is surprisingly large compared with that observed in other experiments and is related to the long lifetime of the lower level (metastable) $^3P_2$ of the transition. In this level, hard-sphere collisions give rise to velocity changes which are comparable to the thermal velocity but, moreover, metastability-exchange processes are expected to occur. During such processes, active atoms of a given longitudinal velocity exchange their excitation with ground-state ones having arbitrary longitudinal velocity within the thermal distribution. One collision, on average, is thus practically sufficient to thermalize the distribution. In a previous experiment using a single laser and isotopically pure krypton, it was not possible to discriminate between the effect of metastability exchanges and the effect of elastic velocity-changing collisions (vcc). The net rate of thermalizing events only could be determined.[5]

The aim of this paper is to show that, by use of a two-laser experiment performed in isotopic mixtures, this discrimination becomes possible. Application to ^{86}Kr-^{78}Kr mixtures has led to the determination of the metastability-exchange cross section between $(^3P_2)$Kr atoms and $(^1S_0)$Kr atoms.

II. SUMMARY OF PREVIOUS RESULTS[5]

The previous experiment was performed in pure ^{86}Kr and in ^{86}Kr-Xe mixtures, the recorded saturated-absorption profiles showing the large Gaussian background superimposed on the narrow resonance. Measurements of their relative magnitude G/L (G = Gaussian amplitude, L = Lorentzian amplitude) for different partial pressures and vanishing saturation led to the determination of the total rate of thermalizing events Γ_1 through the simple relation

$$G/L = 2\sqrt{\pi}\,(\ln 2)^{1/2}\frac{\tilde{\gamma}}{\Delta\nu_D}\,\frac{\Gamma_1}{\gamma}$$

where $\tilde{\gamma}$ is the homogeneous width, $\Delta\nu_D$ the Doppler one, and $1/\gamma$ the lifetime of active atoms. Measurements performed in pure Kr showed that the interaction time of atoms with the electromagnetic fields is limited by the diameter of the laser beams (transit time); in Kr-Xe mixtures, the interaction time is limited by the quenching of Kr metastables by Xe atoms. The value of $\Gamma_1 = (1.8 \times 10^4 p$, where p is in mTorr and Γ_1 in s^{-1}) was calculated from the value of the quenching cross section (70 Å^2) which was estimated from measurements performed at higher temperatures.[14] However, this cross section has been measured recently at room temperature, to 46 Å^2 (Ref. 15); with this new value, the rate of thermalizing events should be $\Gamma_1 = 1.2 \times 10^4 p$ mTorr s^{-1}, with an accuracy probably not better than 10%.

III. PRINCIPLE OF THE PRESENT EXPERIMENT

A first dye laser beam at fixed frequency is used to saturate the absorption on the 557-nm transition of Kr I ($4p^5 5s[\frac{3}{2}]_2$–$4p^5 5p'[\frac{1}{2}]_1$) and a second tunable dye laser is used to probe the nonlinear absorption. The two beams counterpropagate in a discharge tube filled with ^{86}Kr and ^{78}Kr. The saturating beam is chopped at an audio frequency and phase-sensitive detection is used on the probe. The saturating beam is locked off-resonance for ^{86}Kr, so that only a given subclass of longitudinal velocity is pumped for ^{86}Kr, without substantial pumping of ^{78}Kr. This excitation is achieved using the isotope shift of the 557-nm line of Kr I (Ref. 16) (see Fig. 1). Therefore the probe beam sees the response corresponding to ^{86}Kr atoms that have undergone thermalizing collisions (whatever is their nature) and the response corresponding to ^{78}Kr atoms that have undergone exchange collisions with ^{86}Kr.

Recordings obtained for various partial pressures of the two isotopes have revealed that the corresponding backgrounds are fairly well interpreted as Gaussian profiles characterized by the Doppler width, for ^{86}Kr as well as for ^{78}Kr. From their relative magnitude, it is thus expected to gain information on the two mechanisms which are responsible for their formation, i.e., thermalizing collisions acting on the metastable level of ^{86}Kr and exchange collisions between ^{86}Kr and ^{78}Kr.

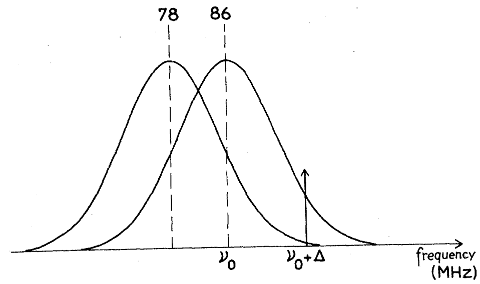

FIG. 1. Schematic representation of the relative position of the line profiles corresponding to ^{86}Kr and ^{78}Kr. The isotope shift is 363 MHz; pumping is performed at $\Delta = 500$ MHz away from ^{78}Kr.

IV. CALCULATION OF THEORETICAL PROFILES

To calculate the saturated-absorption profiles which are expected in isotopic mixtures, we consider the rate equations which govern the evolution of the populations in the excited states of ^{86}Kr and ^{78}Kr. Steady-state populations in the metastable level can be written, in an intuitive form, as the following:

$$\begin{aligned}0=\frac{dn_{86}^*(v)}{dt}&=-(\gamma+\Gamma^{\mathrm{vcc}}+\Gamma^M+\Gamma'^E)n_{86}^*(v)+\Gamma^{\mathrm{vcc}}\frac{e^{-v^2/u^2}}{u\sqrt{\pi}}\int n_{86}^*(v')dv'+\Gamma^M\frac{e^{-v^2/u^2}}{u\sqrt{\pi}}\int n_{86}^*(v')dv'\\&\quad+\Gamma^E\frac{e^{-v^2/u^2}}{u\sqrt{\pi}}\int n_{78}^*(v')dv'+P(v-v_1)\,,\\0=\frac{dn_{78}^*(v)}{dt}&=-(\gamma+\Gamma^E)n_{78}^*(v)+\Gamma'^E\frac{e^{-v^2/u^2}}{u\sqrt{\pi}}\int n_{86}^*(v')dv'\,.\end{aligned}\qquad(1)$$

The first term in parentheses represents the loss of atoms at velocity (v); $1/\gamma$ is the radiative lifetime or any time of interaction (noncollisional) shorter than $1/\gamma$. The rates Γ^{vcc}, Γ^M, Γ'^E, and Γ^E are the rates for vcc, metastability exchanges and exchanges between ^{86}Kr and ^{78}Kr. Note that Γ^{vcc} is proportional to the total pressure, Γ^M and Γ^E are proportional to ^{86}Kr pressure, and Γ'^E is proportional to ^{78}Kr pressure. The second, third, and fourth terms are "incoming" terms at velocity v, from vcc, metastability exchanges, and exchanges between isotopes. The form under which they are expressed indicates that we assume a "strong" collision model leading to Gaussian backgrounds having the Doppler width; in other words, an atom after one collision on average has lost the memory of its initial velocity. $P(v-v_1)$ is the pumping term due to the saturating laser beam; here we assume that it is represented by a Lorentzian of width $\tilde{\gamma}/k$ [full width at half maximum (FWHM)] and intensity L; the velocity v_1 is related to the detuning Δ of the pump laser by $\Delta = kv_1$ where k is the wave vector. The relation (1) for ^{78}Kr contains fewer terms, due to the absence of pumping by the saturator and to the fact that vcc and metastability-exchange collisions do not alter the thermal ^{78}Kr distribution.

By integration over velocities, one obtains

$$0=\frac{dn_{86}^*}{dt}=P-\gamma n_{86}^*-\Gamma'^E n_{86}^*+\Gamma^E n_{78}^*\,,$$
$$0=\frac{dn_{78}^*}{dt}=-\gamma n_{78}^*-\Gamma^E n_{78}^*+\Gamma'^E n_{86}^*\,, \tag{2}$$

where $\int n_{86}^*(v)dv=n_{86}^*$ is the total population in the metastable level and $P=\int P(v-v_1)\,dv$ is the total pumping rate. We can rewrite Eq. (1) with the values of n_{86}^* and n_{78}^* deduced from Eqs. (2) to obtain

$$n_{86}^*(v)=\frac{1}{\gamma+\Gamma^{\text{vcc}}+\Gamma^M+\Gamma'^E}\left(\frac{(\Gamma^{\text{vcc}}+\Gamma^M)(\gamma+\Gamma^E)+\Gamma^E\Gamma'^E}{\gamma+\Gamma^E+\Gamma'^E}\frac{P}{\gamma}e^{-v^2/u^2}+P(v-v_1)\right),$$
$$n_{78}^*(v)=\frac{\Gamma'^E}{\gamma+\Gamma^E+\Gamma'^E}\frac{P}{\gamma}e^{-v^2/u^2}. \tag{3}$$

From expressions (3), one easily sees that the response corresponding to ^{86}Kr atoms appears as a Gaussian background centered at $v=0$ and a Lorentzian resonance centered at velocity v_1. The response corresponding to ^{78}Kr atoms is a Gaussian background only, centered at $v=0$. Therefore the probe beam signal is the sum of the two backgrounds shifted by an amount equal to the isotope shift, plus the narrow resonance (FWHM: $2\tilde{\gamma}$) centered at $-\Delta$ (the pump-laser frequency is locked at $+\Delta$ off-resonance for ^{86}Kr during scanning of the probe. The two beams counterpropagate in the cell).

Experimentally, the quantities of interest that we can estimate are the relative intensities of the three components, i.e., the quantities $G_{86}(v=0)/L_{86}(v=v_1)$ and $G_{78}(v=0)/L_{86}(v=v_1)$. Under the assumption that $\Gamma^E=\Gamma^M$, which seems reasonable with regard to the very small energy difference between the levels associated to the two isotopes,[16] we obtain these quantities in the simple form

$$\frac{G_{86}}{L_{86}}=\frac{\tilde{\gamma}\sqrt{\pi}}{ku}\left[\frac{\Gamma^M}{\gamma}\left(1+\frac{\Gamma^{\text{vcc}}}{\gamma+\Gamma^E+\Gamma'^E}\right)+\frac{\Gamma^{\text{vcc}}}{\gamma+\Gamma^E+\Gamma'^E}\right],$$
$$\frac{G_{78}}{L_{86}}=\frac{\tilde{\gamma}\sqrt{\pi}}{ku}\left[\frac{\Gamma'^E}{\gamma}\left(1+\frac{\Gamma^{\text{vcc}}}{\gamma+\Gamma^E+\Gamma'^E}\right)\right]. \tag{4}$$

By setting $\Gamma'^E=0$ in expressions (4), one regains the expression of G/L which was obtained for pure isotopic Kr in Ref. 5. Furthermore, expressions (4) imply that it is convenient to work at a fixed total pressure and variable partial ones in measuring the G/L's. In effect, in our experiment $1/\gamma$ has to be replaced by the time during which active atoms stay in the light beams. This time depends on the geometry of the beams and on the total pressure in the cell. It can be expressed as $1/\gamma=w_0^2/\bar{\lambda}\bar{v}$ where w_0 is the beam waist, $\bar{\lambda}$ the mean free path of particles, and $\bar{v}$ a mean relative velocity. $\bar{\lambda}$ can be calculated from kinetic theory by taking for the rate of collisions the total rate of thermalizing events.[6,7] $1/\gamma$ is thus constant for a constant total pressure. Furthermore, we can assume that the rate of exchange collisions is the same in the sense $^{86}\text{Kr}\rightarrow{}^{78}\text{Kr}$ as in the sense $^{78}\text{Kr}\rightarrow{}^{86}\text{Kr}$, leading to $\Gamma^E+\Gamma'^E=(\text{const})$ for a constant total pressure. Accordingly, G/L's appear as linear functions of partial pressures, with the same slope for both isotopes. For ^{86}Kr, the ordinate at $p_{86}=0$ depends on vcc, whereas for ^{78}Kr the ordinate at $p_{78}=0$ is equal to 0.

V. ANALYSIS OF THE EXPERIMENTAL DATA

A. Experiments in pure isotopic Kr

In the perspective of determining again the total rate of thermalizing events and the value of $1/\gamma$, we have performed a series of measurements in pure ^{86}Kr as in Ref. 5, but using two lasers. Measurements of G/L have been made for $\Delta=0$ and 500 MHz (frequency units) in the range 20–100 mTorr of Kr pressure. We observe then a quadratic variation of G/L with pressure, as is shown in Fig. 2 on log-log scales. (Note the straight line of slope 2.) This is easily understood, since we can write

$$G/L=\sqrt{\pi}(\ln 2)^{1/2}\frac{2\tilde{\gamma}}{\Delta\nu_D}\frac{\Gamma_1}{\gamma}$$

as in Ref. 5, where $\Delta\nu_D$ is the total Doppler width (720 MHz) and Γ_1 is the rate of thermalizing events. This expression for G/L is also supported by Eqs. (4) where Γ'^E is set equal to 0. From Eqs. (4) we obtain

$$G/L=\sqrt{\pi}(\ln 2)^{1/2}\frac{2\tilde{\gamma}}{\Delta\nu_D}\frac{\Gamma^M+\Gamma^{\text{vcc}}}{\gamma}$$

implying that $\Gamma_1=\Gamma^M+\Gamma^{\text{vcc}}$. Γ_1 and $1/\gamma$ are proportional to pressure. We can write $\Gamma_1=ap$ and $1/\gamma=(w_0^2/\bar{v}^2)\sqrt{2}\,\Gamma_1$.[6,7] $2\tilde{\gamma}$ is here practically constant. [Through our measurements, $2\tilde{\gamma}$ is determined by the homogeneous width broadened by saturation, by the contribution due to vcc occurring at large impact parameters ("weak" vcc), and by the jitter of the lasers. We observed no significant variations of $2\tilde{\gamma}$ in the range of pressure and consequently we have taken a mean value of $2\tilde{\gamma}\approx 50$

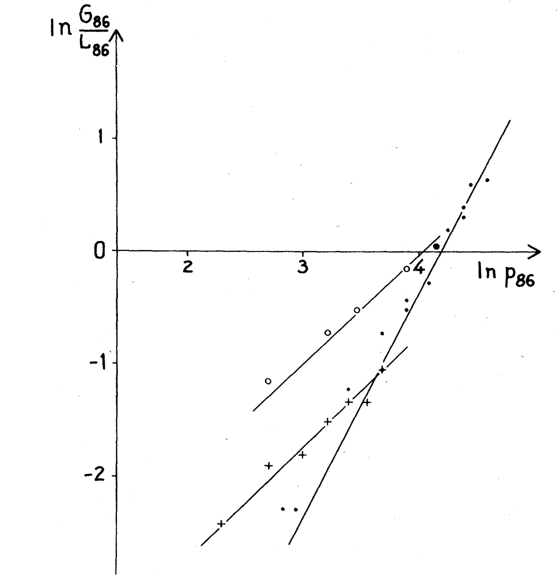

FIG. 2. Log-log plot of (G_{86}/L_{86}) as a function of p_{86}. Points correspond to the experiment performed in pure ^{86}Kr (slope 2), circles and crosses correspond to the experiments performed in ^{86}Kr-^{78}Kr mixtures at total pressures of 65 and 40 mTorr, respectively (slope 1).

MHz.] From our measurements of G/L we deduce $\Gamma_1 = 1.45 \times 10^4 p$ mTorr s^{-1} and $1/\gamma = 0.14 \times 10^{-6} p$, where p is expressed in mTorr and $1/\gamma$ in s. This is, of course, the net rate of thermalizing events, with no possibility to determine the relative contribution of metastability exchanges and elastic vcc. It is to be compared with the rate $1.2 \times 10^4 p$ mTorr s^{-1} that we have deduced from Refs. 5 and 15 (see summary of previous results). These two values are in rather good agreement with respect to the various assumptions used in calculating $1/\gamma$ and to the uncertainty in measuring w_0 (~1 mm).

B. Experiments in isotopic mixtures

Measurements have been performed in ^{86}Kr - ^{78}Kr mixtures as explained above, with a detuning $\Delta = 500$ MHz off resonance for ^{86}Kr and no pumping of ^{78}Kr atoms. Recorded profiles obtained at constant total pressures and various partial pressures have been interpreted in terms of expressions (3). Fits have been made by adjusting only one parameter, the relative magnitude of the Gaussian curves. Figure 2 shows the results obtained for (G_{86}/L_{86}) variations, for two values of the total pressure, 40 and 65 mTorr. One sees immediately that the slope of the straight lines is now equal to 1, indicating that, as expected, $1/\gamma$ is determined by the total pressure. In Fig. 3(a) are plotted the variations of G_{86}/L_{86} versus pressure of ^{86}Kr in linear coordinates, and in Fig. 3(b) are plotted the variations of G_{78}/L_{86} versus pressure of ^{78}Kr.

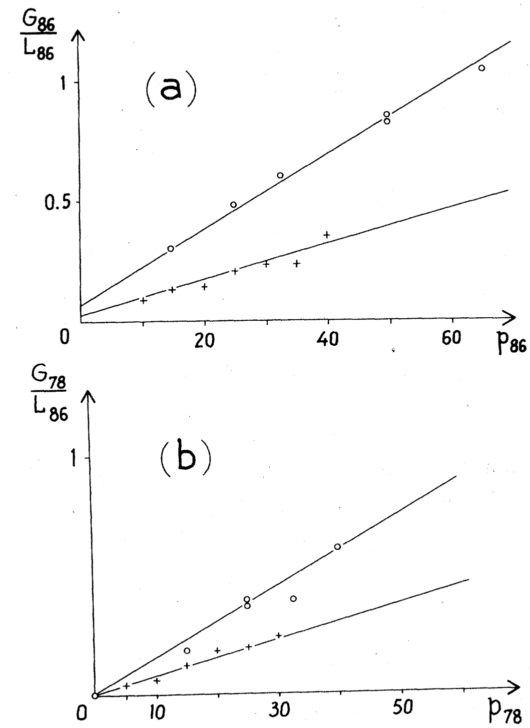

FIG. 3. Variations of (G_{86}/L_{86}) vs p ^{86}Kr, (a) and (G_{78}/L_{86}) vs p ^{78}Kr, (b) in linear coordinates. Circles and crosses correspond to total pressures of 65 and 40 mTorr, respectively.

The linear variations of G/L expected from (4) are clearly established for both isotopes and for both total pressures. The slopes, at a given total pressure, are identical for both isotopes. Furthermore, the ordinate at $p_{86} = 0$ is nonzero for ^{86}Kr, whereas it vanishes for ^{78}Kr. Consequently we can ascertain that expressions (4) represent the physical phenomena fairly well.

Furthermore, we can check the self-consistency of the results in the following manner. By writing

$$2\tilde{\gamma}\sqrt{\pi}\,(\ln 2)^{1/2}/\Delta\nu_D = K$$

and

$$\Gamma^{\text{vcc}}/(\gamma + \Gamma^E + \Gamma'^E) = X(P)$$

$[X(P) \equiv X$ for the total pressure of 65 mTorr and $X(P) \equiv X'$ for the total pressure of 40 mTorr$]$ one can express G/L in the simplified form

$$G_{86}/L_{86} = K\{(\Gamma^M/\gamma)[1 + X(P)] + X(P)\}, \qquad G_{78}/L_{86} = K(\Gamma'^E/\gamma)[1 + X(P)]. \tag{5}$$

We can evaluate directly X and X' from the measurement of the ordinates at the origin [for ^{86}Kr, Fig. 3(a)] and compare $(1+X)/(1+X')$ with the value that we can deduce from measurements of the slopes α in Fig. 3(a). From the intercepts we obtain $KX=0.07$; $KX'=0.03$ which, using the value $K=0.11$ gives $(1+X)/(1+X')$ (intercept) $=1.285$. From the slopes, we find

$$\frac{\alpha\ (P=65)}{\alpha'\ (P=40)}=2.14=\frac{65}{40}\ \frac{1+X}{1+X'}\ ;$$

hence

$$\frac{1+X}{1+X'}\ (\text{slopes})=1.317\,.$$

Thus the agreement seems very good but it may be fortuitous since measurements of the intercepts are less accurate than those of the slopes α and α'. However, the only assumption made here is that $1/\gamma$ is proportional to total pressure.

We are able now to deduce the value of Γ^M from our measurements. This is easily performed by introducing the measured values of X and X' into the measured values of α and α' (5). Then one only needs the value of $1/\gamma$ for each total pressure, easily deduced from the measurements performed in pure ^{86}Kr. Doing that we obtain $\Gamma^M = 0.93\times10^4 p$ mTorr s^{-1}.

VI. DISCUSSION

We have obtained $\Gamma_1=1.45\times10^4 p$ mTorr s^{-1} for the net rate of thermalizing events (from experiments in pure ^{86}Kr) and $\Gamma^M=0.93\times10^4 p$ mTorr s^{-1} for the rate of metastability exchanges (from experiments in isotopic mixtures). As we have seen before, we can evaluate now the rate Γ^{vcc} for velocity-changing collisions by writing $\Gamma_1=\Gamma^M+\Gamma^{vcc}$. We obtain $\Gamma^{vcc}=0.52\times10^4 p$ mTorr s^{-1}. This rate is very close to the rate of collisions in a hard-sphere model $\Gamma_c=0.48\times10^4 p$ mTorr s^{-1} where the radii of active atoms and perturbers are those measured in the ground state.[17] This confirms the results that were obtained in Refs. 6 and 7 but not those obtained in Ref. 5. In effect, in Ref. 5 Γ^{vcc} was estimated to $1\times10^4 p$ mTorrs^{-1} by taking for the radius of active atoms the radius calculated in the excited $4p^55s$ configuration and Γ^M was estimated to $0.7\times10^4 p$ mTorr s^{-1} from theoretical considerations.[18] Consequently the ratio Γ^{vcc}/Γ^M was estimated to 1.4, whereas we demonstrate here that it is equal to $(0.52\times10^4)/(0.93\times10^4)=0.56$.

From the value $\Gamma^M=0.93\times10^4 p$ mTorr s^{-1} we can easily calculate the cross section for metastability exchanges: $Q=75$ Å^2, with an accuracy which we can estimate, from the consistency of our results, to ±10 Å^2. This value is large compared to the ones measured by optical pumping techniques, in He, Ne, and Xe and equal to 7.5, 18, and 70 Å^2, respectively.[19-22] One can notice, however, that a cross section of 77 Å^2 is obtained when taking for the radius of active atoms the radius calculated in the $4p^55s$ configuration.[23]

VII. CONCLUSION

The use of a two-laser experiment performed in isotopic Kr mixtures has allowed us to determine the value of the metastability-exchange cross section $Q=(75\pm10)$ Å^2. We have confirmed that the rate of vcc can be approximated fairly well by the rate of collisions in a hard-sphere model. The method is based on the assumption that the exchange collisions between the two isotopes have the same rate as the metastability exchanges between identical partners. The accuracy of the measurements could be improved by using a larger beam diameter leading to a more precise determination of the transit time. However, we believe that such experiments performed in other species (Ar, Ne) for which the isotope shift is larger, could lead to a study of the rate of exchanges between isotopes.

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