passed through an electrostatic analyzer and into a silicon surface-barrier detector. The electrostatic analyzer is of a cylindrical design[8] with a 30-cm radius. For charge separation the ion beam is deflected through 117 deg, and after analysis the ions are further collimated by a 6-mm slit before passing into the particle detector. Figure 5 demonstrates the analyzer's resolution.

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Shift and Broadening of the ^{87}Rb 0-0 Line Due to Collisions with Krypton Buffer-Gas Atoms

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The shift and broadening of the ^{87}Rb 0-0 line (frequency 6.8 GHz) due to collisions with Kr atoms have been studied in the pressure range 0.2–10 Torr. The shift versus pressure has been found to be linear and equal to -542 ± 10 Hz/Torr. The linewidth results from the superposition of several effects which are analyzed, one of the most important being the relaxation due to the spin-orbit interaction experienced by Rb atoms while temporarily bound in van der Waals Rb-Kr molecules.

I. INTRODUCTION

The interactions between two colliding atoms are currently the subject of many investigations. Direct observation of the internal degrees of freedom of the colliding partners can provide useful information complementing the results of scattering experiments. Study of the relaxation of polarized ^{87}Rb atoms in krypton buffer gas[1] has thus proved to be very sensitive to the presence of transient bound states in the Rb-Kr pair. In this connection one is led to wonder if the very narrow 0-0 hyperfine line of ^{87}Rb (unperturbed frequency[2] 6 834 682 614 Hz) should not be affected by the same phenomena.

Measurements, using standard optical pumping techniques, of the 0-0 linewidth at 27 °C (Rb vapor pressure 3×10^{-7} Torr) in the presence of various buffer gases (He, Ne, Ar, N_2, CH_4) have already been made, at pressures ranging from 1 to 400 Torr.[3] When only binary collisions between Rb and buffer-gas atoms take place, one expects the linewidth to be the sum of two terms: a collision-narrowed Doppler width, inversely proportional to buffer-gas pressure, and a contribution proportional to the buffer-gas pressure, due to disorienting or dephasing collisions.[4]

Whereas the experimental results agree well with such a prediction in the case of He and Ne, there exists in the cases of Ar, N_2, and CH_4 a small extra linewidth which has been attributed by Bender and Cohen[3] to the formation of bound states.

In view of the relaxation experiments[1] which dem-

onstrated the importance of such bound states in the case of Kr buffer gas, we were led to study the shift and broadening of the ^{87}Rb 0-0 line in the same gas. The shift of this transition due to collisions with Kr had already been determined,[5] but no reliable linewidth measurements had been performed so far. We shall see that such measurements give results in agreement with the conclusions of relaxation studies and the presence of bound states in a Rb-Kr mixture.

II. LONGITUDINAL RELAXATION STUDIES

Let us first recall the results of longitudinal relaxation studies[1] and the numerous conclusions which can be deduced from them.

The atomic system we are considering is the $^2S_{1/2}$ ground state of an alkali atom subjected to a weak magnetic field $\vec{H}_0$. The coupling $A_I\vec{I}\cdot\vec{J}$ between the electronic moment $J=S=\frac{1}{2}$ and the nuclear moment I splits the ground state into two hyperfine levels $F=I+\frac{1}{2}$ and $F'=I-\frac{1}{2}$, separated by the hyperfine interval $\Delta W=A_I(I+\frac{1}{2})$. Under the action of $\vec{H}_0$, these levels are in turn split into Zeeman sublevels with Landé factors $g_F=-g_{F'}=g_S/(2I+1)$. The 0-0 transition of interest to us connects the sublevels $|F, m_F=0\rangle$ and $|F', m_{F'}=0\rangle$, whose energy separation is independent of H_0 in first order and equal to ΔW. In the case of ^{87}Rb, one has $I=\frac{3}{2}$, $F=2$, $F'=1$, $\Delta W/h=6.8$ GHz, and $g_F=700$ kHz/G.

Previous studies of the rubidium ground state in the presence of krypton buffer gas[1] were concerned with the relaxation of sublevels populations.[6] It has been shown that this relaxation was due to the effect of spin-orbit coupling[7] during collisions, and that two types of processes had to be considered: ordinary Rb + Kr collisions,[8] and ternary Rb + Kr + Kr collisions leading to Rb-Kr molecule formation.

A. Ordinary Binary Collisions

Ordinary binary collisions have a very short duration, $\tau_c \sim 10^{-12}$ sec. The average time interval between two successive Rb-Kr collisions is $\tau_V = 1.25 \times 10^{-7}$ sec at 1 Torr. The relevant spin-orbit Hamiltonian is written in Ref. 1 as

$$\mathcal{H}_1' = \gamma(r,t)\,\vec{S}\cdot(\mu\vec{V}\times\vec{b}/\hbar), \tag{1}$$

where $\vec{V}$ is the relative velocity of the colliding atoms and $\vec{b}$ the impact parameter.

It is shown in Ref. 1 that the longitudinal relaxation constants associated with this mechanism may be related to the quantity [Eq. (43) of Ref. 1]

$$1/T_{S1} = (\mu^2/3\hbar^4)\int V^3 b^2 n(\vec{V}) d^2b\, d^3V \left| \int_{-\infty}^{+\infty} \gamma(r(t))dt \right|^2, \tag{2}$$

which experimentally is found to be

$$1/T_{S1} = 32\ \text{sec}^{-1}\times P \qquad (P \text{ in Torr}). \tag{3}$$

B. Rb-Kr Molecules

These bound states arise from ternary collisions. They have a duration T obeying a distribution law of the form $\exp(-T/\tau)$ with $1/\tau = \beta\overline{V}_{Mr}P\bar{\sigma} \propto P$, and the average time interval between the formation of two successive bound states for a particular Rb atom is T_f, such that $1/T_f = \beta^2\overline{V}_{Mr}KP^2\bar{\sigma} \propto P^2$ [Eqs. (72) and (73) of Ref. 1]. Experimentally for ^{87}Rb in Kr one has

$$\tau^{-1} = 1.55\times10^7 P \quad \text{and} \quad T_f^{-1} = 84\times P^2 \quad (P \text{ in Torr}). \tag{4}$$

The spin-orbit coupling in the bound state is

$$\mathcal{H}_1'' = \gamma(r)\,\vec{S}\cdot\vec{N}\ , \tag{5}$$

where $\hbar\vec{N}$ is the relative angular momentum of the Rb-Kr pair.

Since our own experimental uncertainty does not allow very high refinements, the theoretical results of Ref. 1 will here be presented in their simplest form, i.e., we shall in Eq. (5) replace $\gamma(r)$ by some average value γ independent of $|\vec{N}|$.

The average value of $|\vec{N}|$ being large ($\overline{N}=38$), $\vec{N}$ may be treated as a classical vector whose orientation with respect to the external magnetic field $\vec{H}_0$ is arbitrary and whose length has a distribution law given by Eq. (69) of Ref. 1. The effect of the spin-orbit coupling in the bound state is then equivalent to that of an additive magnetic field $\vec{H}_1 = (\gamma\vec{N}/\hbar\gamma_S)$.

The spin-orbit coupling constant is very small compared to the hyperfine interval ($\gamma/h = 0.63$ MHz for Rb-Kr) and τ is very long compared to the hyperfine period. For this reason it is possible, in the relaxation calculations, to replace $\mathcal{H}_1''$ by the truncated Hamiltonian

$$\mathcal{H}_1'' = \textstyle\sum_F P_F(\hbar\gamma_F\vec{F}\cdot\vec{H}_1)P_F, \tag{6}$$

where P_F is a projection operator.

Let us call θ and φ the polar angles for $\vec{H}_1$ with respect to $\vec{H}_0$ and define

$$\omega_1 = \gamma_F|H_1| = \gamma_S|H_1|/(2I+1). \tag{7}$$

The distribution law of ω_1 is given by

$$P(\omega_1)d\omega_1 = \begin{cases} (3/4\overline{\omega}_1^3)\omega_1(2\overline{\omega}_1-\omega_1)d\omega_1, & 0<\omega_1<2\overline{\omega}_1 \\ 0, & \omega_1>2\overline{\omega}_1 \end{cases} \tag{8}$$

with

$$\overline{\omega}_1 = \gamma_F\overline{H}_1 = \gamma\overline{N}/(2I+1)\hbar\ (=2\pi\times6\ \text{MHz for } ^{87}\text{Rb-Kr}). \tag{9}$$

One has $\langle\omega_1\rangle = \overline{\omega}_1$ and $\langle\omega_1^2\rangle = \frac{6}{5}\,\overline{\omega}_1^2$.

We shall be interested here in the case when the external field H_0 is much smaller than $\overline{H}_1$ (but nevertheless nonzero in order that the secular approximation be valid). Then, with the help of the identity

$$\sum_{m'} P(F, m, m', t)m'$$

$$\equiv \sum_{m'} |\langle Fm'|\exp(-i\gamma_F \vec{F}\cdot\vec{H}_1 t)|Fm\rangle|^2 m'$$

$$= m\,[\cos^2\theta + \sin^2\theta\cos(\omega_1 t)], \qquad (10)$$

it is possible to show that the longitudinal relaxation constants may be related to the quantity

$$(1/T_n) = (2/T_f)\langle \sin^2\theta \sin^2 \tfrac{1}{2}\omega_1 T\rangle_{\mathrm{av}\,\theta,T,N}. \qquad (11)$$

After averaging over θ and T this becomes

$$\frac{1}{T_n} = \frac{2}{3}\frac{1}{T_f}\int P(\omega_1)d\omega_1 \frac{(\omega_1\tau)^2}{1+(\omega_1\tau)^2}. \qquad (12)$$

The authors of Ref. 1 introduce reduced units A^* and P^* such that

$$A^* = \tfrac{2}{3}\langle\omega_1^2\rangle\,\tau^2/T_f \text{ and } P^{*2}/P^2 = \langle\omega_1^2\rangle\tau^2. \qquad (13)$$

In terms of these units Eq. (12) finally becomes

$$1/T_n = A^* f(P/P^*), \qquad (14)$$

where the function f, represented in Fig. (11) of Ref. 1, may be calculated to be

$$f(x) = x^2\{1 + \tfrac{9}{5}x^2 - \tfrac{9}{10}x^2\ln[1+(10/3x^2)] - \tfrac{9}{10}\sqrt{\tfrac{6}{5}}\,x^3\tan^{-1}(2\sqrt{\tfrac{5}{6}}\,x^{-1})\}. \qquad (15)$$

When $P \to 0$, $1/T_n \sim \frac{2}{3}(1/T_f) = A^*(P^2/P^{*2})$, and, when $P \to \infty$, $1/T_n \to A^*$. Experimentally for ^{87}Rb-Kr one has

$$A^* = 391.2\ \mathrm{sec}^{-1} \text{ and } P^* = 2.65\ \mathrm{Torr}.$$

Before describing our own experimental results and their interpretation, let us now indicate briefly what are the differences between the above longitudinal relaxation experiments and our study of the 0-0 transition.

First, we are interested in a nondiagonal matrix element, i.e., in an atomic frequency and a transverse relaxation time T_2 which, contrary to the longitudinal observables, are also sensitive to adiabatic perturbations. In our case the adiabatic perturbation of interest is the variation $\delta A_I \vec{I}\cdot\vec{S}$ of the hyperfine interaction during collisions. It is well known that this variation (which has a nonzero average value during the collision) is responsible for the important pressure shift of the 0-0 line in the presence of buffer gases.[9]

Consequently, when we calculate the relaxation and line shift for each collision process (binary or ternary), we shall have to consider two mechanisms: (a) variation of the hyperfine structure and (b) spin-orbit coupling, the effects of which may or may not be separated.

Second, since we measure a linewidth and not a relaxation time, in order to attain the relaxation linewidth $1/\pi T_2$, the collision-narrowed Doppler width[4] will have to be subtracted.

III. MEASUREMENTS ON 0-0 LINE

The present experiments were made using the same apparatus as in Refs. 3 and 5. The resonance cells were sealed-off spherical Pyrex bulbs about 10 cm in diam which were thoroughly outgassed before filling with a few mg of ^{87}Rb and krypton at the desired pressure. They were placed in a magnetically shielded enclosure inside which a pair of Helmholtz coils maintained a magnetic field of 30 mG. The temperature of the cell was 27 °C.[10] Optical pumping was performed by a Varian ^{87}Rb lamp and a ^{85}Rb filter. The 6.8-GHz frequency for the excitation of the 0-0 transition was produced by mixing the 5.3-MHz output of a crystal-controlled frequency synthesizer with the 1368th harmonic of a very high spectral purity quartz oscillator at 5 MHz, which was periodically checked against the U. S. Frequency Standard, located in the same laboratory. The resulting radiation, with a power level of a few μW, was attenuated and sent through a microwave horn onto the cell, which was thus subjected to a traveling plane wave. The amplitude of this radiation was square-wave modulated at 3 Hz, and the resonance was detected by monitoring the resulting intensity modulation of the transmitted pumping light with a lock-in amplifier.

The shift and linewidth of the 0-0 resonance were measured for each cell. The frequency shift $\delta\nu$ shows a linear dependence versus pressure (Fig. 1): We find a value of -542 ± 10 Hz/Torr, which agrees with the previous measurements[5] but has a some-

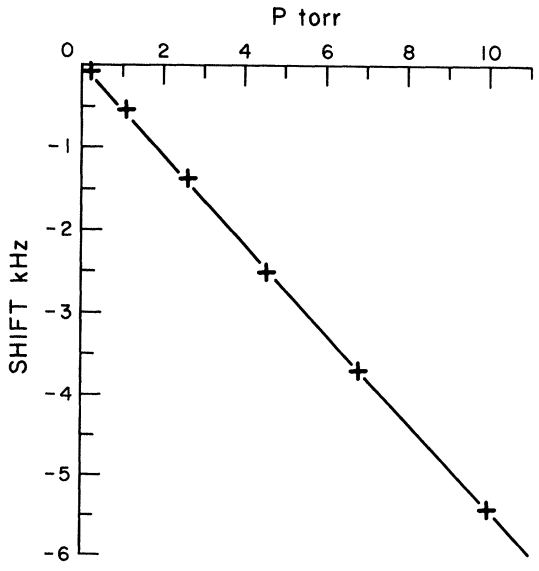

FIG. 1. Frequency shift of the 0-0 transition of ^{87}Rb as a function of Kr buffer-gas pressure.

what higher accuracy.

The experimental determination of the linewidth $\Delta\nu$ versus pressure is rather difficult because of the double extrapolation (to zero light intensity and zero microwave power) needed and the large value of the linewidth in the presence of several Torr of Kr, with the corresponding reduction in signal-to-noise ratio. The values obtained are shown in Fig. 2.

In order to interpret these results, the different contributions to the shift and linewidth – Doppler effect, influence of binary collisions and of molecule formation – have to be analyzed in detail. This is done in Sec. IV.

IV. THEORETICAL ANALYSIS

A. Doppler Effect

In the absence of a buffer gas, the Doppler effect due to the random motion of the rubidium atoms subjected to a traveling wave would give to the 0-0 resonance a Gaussian shape with a width $\Delta\nu_D$ ($\Delta\nu_D$ = 9.1 kHz for ^{87}Rb at 27 °C). As is well known,[4] the diffusive motion of the rubidium atoms in the buffer gas leads to drastic changes from the above situation: The line shape becomes Lorentzian, with a residual width $\Delta\nu_d$ given by the formula

$$\Delta\nu_d = 2.8(L/\lambda)\Delta\nu_D, \tag{16}$$

where λ is the wavelength of the transition under study and L is the transport mean free path, inversely proportional to buffer-gas pressure. In the case of ^{87}Rb in krypton at 27 °C, $L = 6.83\times10^{-3}$ cm at 1 Torr and

$$\Delta\nu_d P \approx 40\ \text{Hz}\times\text{Torr}. \tag{17}$$

The corresponding variation is represented by curve d in Fig. 2.

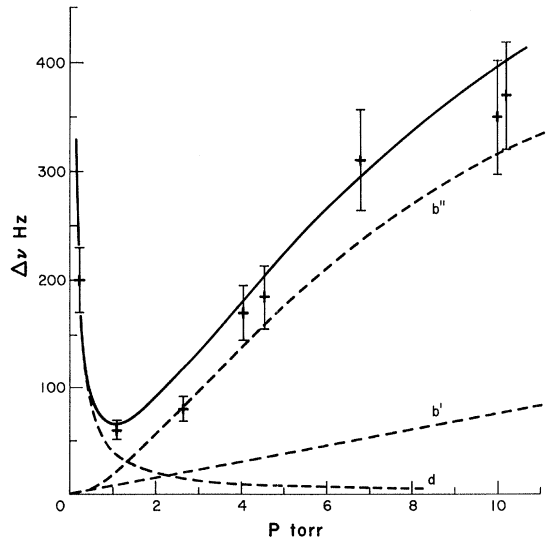

FIG. 2. Linewidth of the 0-0 transition of ^{87}Rb as a function of Kr buffer-gas pressure. Curve d: collision-narrowed Doppler width. Curve b′: binary collisions plus spin-orbit coupling. Curve b″: bound states plus spin-orbit coupling. Solid curve: sum of all contributions.

We must now consider the effect of collisions with the buffer gas on the internal degrees of freedom of the ^{87}Rb atom.[11]

B. Binary Collisions

The collision duration $\tau_c \sim 10^{-12}$ sec being very short, a perturbation approach may be used. In these conditions, the contributions of mechanisms [(a) variation of the hyperfine structure and (b) spin-orbit coupling] to the linewidth and line shift of the 0-0 transition are additive. The fact that the Zeeman interval is assumed to be larger than the different linewidths ensures the validity of the secular approximation.

Mechanism (a). This mechanism gives rise to both a shift and a relaxation. If one defines somewhat crudely an average variation $\hbar\Omega'$ of the hyperfine interval during a collision, then a classical argument leads to

$$\delta\nu_a' = \frac{\Omega'}{2\pi}\frac{\tau_c}{\tau_V},\quad \Delta\nu_a' \equiv \frac{1}{\pi T_{2a}'} = \frac{1}{2\pi}\Omega'^2\frac{\tau_c^2}{\tau_V} = 2\pi(\delta\nu_a')^2\tau_V. \tag{18}$$

$\delta\nu_a'$ and $\Delta\nu_a'$ may also be obtained as a limiting case of Eq. (36) of Sec. IV C ($T_f \to \tau_V$, $\tau \to \tau_c$), but $\Delta\nu_a'$ is then twice as large: This arises from the fact that the first argument assumes that the collision duration has a fixed value τ_c, whereas the second one assumes it obeys a distribution law $\exp(-t/\tau_c)$.

If we suppose that for ^{87}Rb in Kr, the observed shift $\delta\nu = -542$ Hz/Torr is very close to $\delta\nu_a'$ [see Sec. V, Eq. (44)], we obtain

$$\Omega'/2\pi \approx -68\ \text{MHz},\quad \text{whence}\quad \Delta\nu_a' \approx 0.23\ \text{Hz/Torr}. \tag{19}$$

This last value should not be taken too seriously since $\delta\nu_a'$ and $\Delta\nu_a'$ do not indeed measure the same average of the hyperfine interval during the collision. Nevertheless this result as well as the comparison with the effect of other buffer gases,[3] seems to indicate that $\Delta\nu_a' \lesssim 1$ Hz/Torr, which is negligible within our experimental precision.

Mechanism (b). The relevant Hamiltonian $\mathcal{H}_1'$ is given by Eq. (1). The collision duration being very small compared to both Zeeman and hyperfine periods, it is easy to show that the equation of motion of the density matrix σ is

$$\frac{d\sigma}{dt} = -\frac{i}{\hbar}[\mathcal{H}_0,\sigma] - \frac{n}{\hbar^2}\int_{-\infty}^{+\infty} dt' \times\int_{-\infty}^{t'} dt''\,[\mathcal{H}_1'(t'),[\mathcal{H}_1'(t''),\sigma(t)]], \tag{20}$$

where $\mathcal{H}_0$ is the unperturbed Hamiltonian and n the number of collisions per second.

Here we are interested in the $F0 \rightleftarrows F'0$ transition. By the secular approximation, $\sigma_{F0,F'0}$ is decoupled from all other matrix elements. In addition $\langle F0|\mathcal{H}_1'|F0\rangle = \langle F'0|\mathcal{H}_1'|F'0\rangle = 0$. This leads to

$$\frac{1}{T_{2b}'} + i\delta\omega_b' = \frac{n}{\hbar^2}\int_{-\infty}^{+\infty} dt' \int_{-\infty}^{t'} dt'' \{\langle F0|\mathcal{H}_1'(t')\mathcal{H}_1'(t'')|F0\rangle + \langle F'0|\mathcal{H}_1'(t'')\mathcal{H}_1'(t')|F'0\rangle\}_{av\,\vec{v},\vec{b}} \quad (21)$$

in which one must average over the parameters $\vec{v}$ and $\vec{b}$ of the collision. Finally

$$\delta\omega_b' = 0, \quad (22)$$

$$\frac{1}{T_{2b}'} = S(S+1)\frac{1}{T_{S1}} = \frac{3}{4}\frac{1}{T_{S1}}, \quad (23)$$

where $1/T_{S1}$ is given by Eq. (2). One then predicts that

$$\Delta\nu_b' = 1/\pi T_{2b}' = 7.6 \text{ Hz/Torr} \quad (24)$$

(curve b′ on Fig. 2).

C. Rb-Kr Bound States

In this case one goes from a strong collision situation at low pressure (τ long) to a weak collision limit at high pressure (τ short). In the strong collision limit, effects of mechanisms (a) and (b) cannot be separated and must be treated simultaneously.

(i) *General formulas.* As in Ref. 1 we shall consider a time interval t, $t+\Delta t$ such that $\tau \ll \Delta t \ll T_f$. During Δt, a fraction $1 - \Delta t/T_f$ of the atoms remains free, and a fraction $\Delta t/T_f$ enters a molecular Rb-Kr bound state which lasts from t_0 to t_0+T. At the end of the calculation we shall have to average over t_0 and T.

The unperturbed Hamiltonian is

$$\mathcal{H}_0 = A_I\vec{I}\cdot\vec{S} + \hbar\gamma_S S_z H_0 \quad (25)$$

and the perturbed Hamiltonian is

$$\mathcal{H} = (A_I + \delta A_I'')\vec{I}\cdot\vec{S} + \hbar\gamma_S S_z H_0 + \gamma\vec{S}\cdot\vec{N}\ . \quad (26)$$

They may be replaced, respectively, by the truncated Hamiltonians

$$\mathcal{H}_0 = \sum_F P_F\,\mathcal{H}_0 P_F,$$

with

$$P_F\mathcal{H}_0 P_F = E_F + \hbar\gamma_F F_z H_0, \quad (27)$$

$$\mathcal{H} = \sum_F P_F\mathcal{H}P_F,$$

with

$$P_F\mathcal{H}P_F = E_F + \delta E_F + \hbar\gamma_F\vec{F}\cdot(\vec{H}_0 + \vec{H}_1). \quad (28)$$

Calling U_0 and U the evolution operators associated with $\mathcal{H}_0$ and $\mathcal{H}$, the density matrix at $t+\Delta t$ is related to the density matrix at t by

$$\sigma(t+\Delta t) = (1-\Delta t/T_f)U_0(\Delta t)\sigma(t)U_0^*(\Delta t) + (\Delta t/T_f)U_0(t+\Delta t-t_0-T)U(T)U_0(t_0-t)\sigma(t)[U_0(t+\Delta t-t_0-T)U(T)U_0(t_0-t)]^\dagger. \quad (29)$$

With respect to the eigenvectors of $\mathcal{H}_0$ this becomes

$$\Delta t^{-1}\{\exp[(i/\hbar)(E_a^0-E_b^0)\Delta t]\sigma_{ab}(t+\Delta t) - \sigma_{ab}(t)\} = -T_f^{-1}(1-\exp[(i/\hbar)(E_a^0-E_b^0)T]\langle a|\exp[-(i/\hbar)\mathcal{H}T]|a\rangle\{\langle b|\exp[-(i/\hbar)\mathcal{H}T]|b\rangle\}^*)\sigma_{ab}(t) + T_f^{-1}\sum_{a',b'\neq a,b}\exp[(i/\hbar)(E_a^0-E_b^0)T]\exp[(i/\hbar)(E_a^0-E_b^0-E_{a'}^0+E_{b'}^0)(t_0-t)]U_{aa'}(T)U_{bb'}^*(T)\sigma_{a'b'}(t), \quad (30)$$

where one must average over T, t_0 ($t<t_0<t+\Delta t$), and $\vec{H}_1$. From this equation it follows that if the matrix element σ_{ab} is decoupled from all others, its relaxation time is

$$T_{ab}^{-1} = \mathrm{Re}\,T_f^{-1}\left(1-\exp[(i/\hbar)(E_a^0-E_b^0)T]\langle a|\exp[-(i/\hbar)\mathcal{H}T]|a\rangle\{\langle b|\exp[-(i/\hbar)\mathcal{H}T]|b\rangle\}^*\right)_{\mathrm{av}\,T,\vec{H}_1}. \quad (31)$$

Let us now examine the decouplings for the actual system with eigenfunctions of the type $|Fm_F\rangle$. It is easy to show by averaging over the polar angle φ of $\vec{H}_1$ that matrix elements with different $(m_F - m_{F'}')$ are decoupled. As for the decoupling of matrix elements with the same $m_F - m_{F'}'$, one must rely on time-constants considerations. It then appears that two matrix elements ρ_{ab}, $\rho_{a'b'}$ will be decoupled only if the difference between their frequencies $\hbar^{-1}(E_a^0 - E_b^0 - E_{a'}^0 + E_{b'}^0)$ is much larger than quantities like T_{ab}^{-1} [the proof relies on the fact these quantities are $\gtrsim T_f^{-1}$, and that when they are of order T_f^{-1}, T_f is very long

– see Eqs. (14) and (39)].

The practical conclusion is that when the external field is chosen in such a way that the Zeeman splitting is much larger than the hyperfine linewidths, the hyperfine coherences are decoupled from one another, and also from the populations and Zeeman coherences (secular approximation).

(ii) *Linewidth and shift of the* 0-0 *transition.* Let $\hbar\Omega'' = \delta A_I''(I+\frac{1}{2})$ be the variation of the hyperfine interval in the bound state (we assume for simplicity that it does not depend on v and N). Formally it follows from the preceding considerations that the linewidth and line shift of the 0-0 transition under the combined effects of mechanisms (a) and (b) are given by

$$(1/T_2'') + i\delta\omega'' = (1/T_f)\{1 - \exp(-i\Omega'' T) \times \langle F0 | \exp(-i\gamma_F \vec{F}\cdot\vec{H}T)|F0\rangle \times \langle F'0 | \exp(-i\gamma_{F'}\vec{F}'\cdot\vec{H}T)|F'0\rangle\}_{\text{av } T,\vec{N}}\ , \quad (32)$$

where $\vec{H} = \vec{H}_0 + \vec{H}_1$ and the average is over T and $\vec{N}$. We shall assume once more that $H_0 \ll \bar{H}_1$ ($= 8.5$ G for ^{87}Rb-Kr). Quantities like $\langle F0|\exp(-i\gamma_F\vec{F}\cdot\vec{H}_1 T)|\times F0\rangle$ may be evaluated with the help of rotation coefficients:

$$\langle F0|\exp(-i\gamma_F\vec{F}\cdot\vec{H}_1 T)|F0\rangle = \frac{4\pi}{2F+1}|Y_F^0(\theta,0)|^2 + \frac{8\pi}{2F+1}\sum_{M=1}^{F}|Y_F^M(\theta,0)|^2\cos(M\omega_1 t) \quad (33)$$

and depend on the isotope considered. For this reason we shall first examine two limiting cases giving simple formulas which are valid for all isotopes.

First, for high pressures (τ short, weak collision limit) expression (32) must reduce to the result of a perturbation calculation which leads to

$$\frac{1}{T_2''} + i\delta\omega'' = \tfrac{1}{3}\langle\omega_1^2\rangle\frac{\tau^2}{T_f}[F(F+1)+F'(F'+1)] + \frac{\Omega''^2\tau^2}{T_f} + \frac{i\Omega''\tau}{T_f}\ , \quad (34)$$

$$\frac{1}{T_2''} + i\delta\omega'' = \tfrac{1}{6}\gamma_S^2\langle H_1^2\rangle\frac{\tau^2}{T_f} + \frac{\delta A_I''^2(I+\frac{1}{2})^2\tau^2}{\hbar^2 T_f} + i\frac{\delta A_I''(I+\frac{1}{2})\tau}{\hbar T_f} \quad (35)$$

Since $1/T_f \propto P^2$ and $\tau \propto 1/P$, these formulas show that for high P the linewidth tends towards a constant, while the shift is linear in P. Also, as for binary collisions, the spin-orbit contribution does not depend on the isotope (here this is true only at high pressure).

Second, when $\Omega'' \gg \bar{\omega}_1$, expression (32) reduces, as it should, to

$$\frac{1}{T_2''} + i\delta\omega'' = \frac{1}{T_f}\frac{\Omega''^2\tau^2 + i\Omega''\tau}{1+\Omega''^2\tau^2}\ , \quad (36)$$

leading to a shift which is linear at high pressure, as already noted, and vanishes like P^3 at low pressures.

Let us now turn to the specific case of ^{87}Rb ($F=2$, $F'=1$). If we set $G(x) = (x^2+ix)/(1+x^2)$, we deduce from (32) that

$$(1/T_2'') + i\delta\omega'' = (1/T_f)\langle \tfrac{23}{105}G(\Omega''\tau) + \tfrac{23}{105}G((\Omega''+\omega_1)\tau) + \tfrac{23}{105}G((\Omega''-\omega_1)\tau) + \tfrac{9}{105}G((\Omega''+2\omega_1)\tau) + \tfrac{9}{105}G((\Omega''-2\omega_1)\tau) + \tfrac{9}{105}G((\Omega''+3\omega_1)\tau) + \tfrac{9}{105}G((\Omega''-3\omega_1)\tau)\rangle_{\text{av } P(\omega_1)}\ , \quad (37)$$

where the average is now over ω_1.

The physical discussion of Sec. V will show that for ^{87}Rb-Kr molecules, Ω'' is apparently much smaller than $\bar{\omega}_1$. In this case, neglecting Ω'', the integration of the right-hand side of Eq. (37) leads to a rather simple analytical expression; indeed, using the same reduced units as in Ref. 1 one finds

$$\delta\omega'' \equiv \delta\omega_b'' = 0, \quad (38)$$

$$\frac{1}{T_2''} \equiv \frac{1}{T_{2b}''} = A^*\left[\frac{23}{35}f\left(\frac{P}{P^*}\right) + \frac{36}{35}f\left(\frac{P}{2P^*}\right) + \frac{81}{35}f\left(\frac{P}{3P^*}\right)\right]. \quad (39)$$

This is to be compared with Eq. (14);

$$1/T_n = A^* f(P/P^*).$$

When $P \to \infty$, one obtains $1/T_{2b}'' \to 4A^* = \frac{8}{3}(\langle\omega_1^2\rangle\tau^2/T_f)$, in agreement with Eq. (34), while $1/T_n \to A^*$. When $P \to 0$, $1/T_{2b}'' \to \frac{82}{105}(1/T_f)$ while $1/T_n \to \frac{2}{3}(1/T_f)$. Let us recall that for ^{87}Rb, $A^* = 391.2$ sec^{-1} and $P^* = 2.65$ Torr.

V. COMPARISON WITH EXPERIMENT

The experimental linewidth $\Delta\nu$ of the 0-0 transition is represented by the points of Fig. 2. It is seen that when one subtracts from it the Doppler width (curve d) and the contribution of binary collisions (curve b'), the contribution of molecular states $\Delta\nu'' = \Delta\nu_{\text{expt}} - \Delta\nu_d - \Delta\nu_b'$ varies monotonically from 0 to about 320 Hz between 0 and 10 Torr. In the same pressure domain the shift $\delta\nu$ is perfectly linear:

$$\delta\nu = -542 \pm 10 \text{ Hz/Torr}.$$

We shall now show that these facts can be explained only if the hyperfine-structure change $|\hbar\Omega''|$ in the ^{87}Rb-Kr molecules is much smaller than the average change $|\hbar\Omega'|$ during binary collisions, and also smaller than the spin-orbit coupling $\hbar\bar{\omega}_1$ in the

same molecule.

Let us recall that for ^{87}Rb in Kr:

$\tau_c \sim 10^{-12}$ sec (duration of binary collisions),

$\tau_V = 1.25\times10^{-7}/P$ (time of flight of Rb atoms),

$1/\tau = 1.55\times10^{7}P$ (τ is the lifetime of the molecules),

$1/T_f = 84P^2$ (T_f is the time of formation of the molecules),

$\bar{\omega}_1/2\pi = 6$ MHz.

At 10 Torr the frequency $\Omega/2\pi$ for which $\Omega\tau = 1$ is equal to 24.6 MHz. Let us first assume that $\Omega'' \gg \bar{\omega}_1$. Then the shift, taking into account both binary collisions and molecular states, is given by

$$\delta\omega \equiv 2\pi\delta\nu = \delta\omega_a' + \delta\omega_a'' = \Omega'\frac{\tau_c}{\tau_V} + \frac{1}{T_f}\frac{\Omega''\tau}{1+\Omega''^2\tau^2}, \quad (40)$$

and the linewidth associated with molecular states is given by

$$\Delta\omega'' = 2\pi\Delta\nu'' = \Delta\omega_a'' = \frac{2}{T_f}\frac{\Omega''^2\tau^2}{1+\Omega''^2\tau^2}. \quad (41)$$

The experimental shift is a linear function of P while the second term $\delta\omega''$ in Eq. (40) is nonlinear. This contradiction can be solved if either $|\Omega''\tau| \ll 1$ or the second term is negligible with respect to the first, i.e., $|\Omega''\tau| \gg 1$.

Let us now try to fit the values of $\delta\omega$ and $\Delta\omega''$ at 10 Torr using the corresponding value of τ, $\tau_{10} = 0.645\times10^{-8}$ sec. If we use values of Ω'' such that $|\Omega''\tau_{10}| \ll 1$, then the nonlinearity of the shift should occur below 10 Torr and be observable if it is not too small (Ω'' not too small). If we use values of Ω'' such that $|\Omega''\tau_{10}| \gg 1$ then the nonlinearity of the shift occurs above 10 Torr and is unobservable.

We have reason to think that $|\Omega''| \lesssim |\Omega'|$. Assume to begin with that $\Omega'' = \Omega'$. Then from the experimental value $(\delta\nu)_{10\ \mathrm{Torr}} = -5420$ Hz, one deduces $\Omega'/2\pi = \Omega''/2\pi = -62$ MHz, $(\delta\nu'')_{10} = -458$ Hz, and $(\Delta\nu'')_{10} = 2310$ Hz. This linewidth is much too large ($\Delta\nu''_{\mathrm{expt}} \approx 300$ Hz at 10 Torr). Also $|\Omega''\tau_{10}| \sim 2.52$, i.e., $P = 10$ Torr would be in the middle of the nonlinearity zone of $\delta\nu''$ and this nonlinearity should be observable since the predicted value of $\delta\nu''$ at 10 Torr is larger than the experimental error at this pressure (100 Hz). These conclusions would remain true if one had $\Omega''/2\pi \approx +60$ MHz.

If we now take $|\Omega''/2\pi| = 20$ MHz and still neglect $\bar{\omega}_1$ as a first approximation, then at 10 Torr, $|\delta\nu''|_{10} = 656$ Hz, $(\Delta\nu'')_{10} = 1062$ Hz, and $|\Omega''\tau_{10}| = 0.813$. This is still incompatible with experiment.

Assume on the contrary that $|\Omega''| \ll \bar{\omega}_1$. In this case it is possible to demonstrate using Eqs. (37) and (39) that to first order in $(\Omega''/\bar{\omega}_1)$

$$\delta\omega'' = \frac{23}{105}\frac{1}{T_f}\frac{\Omega''\tau}{1+(\Omega''\tau)^2}\left(\frac{82}{105}\frac{1}{T_f} - \frac{1}{T_{2b}''}\right)\Omega''\tau \quad (42)$$

[in which, when $P \to 0$, $(82/105T_f) - 1/T_{2b}'' \sim 1/\tau^2 T_f \sim P^4$]. At 10 Torr using $1/T_f = 8400$, $1/T_2'' = 320\pi$, this gives ($|\Omega''\tau_{10}| \ll 1$)

$$\delta\omega'' = 7400\Omega''\tau_{10}.$$

For the nonlinearity of the pressure dependence of $\delta\omega''$ below 10 Torr to be unobservable, $|\delta\nu''| = |\delta\omega''/2\pi|$ at 10 Torr must be less than 100 Hz. This leads to

$$|\Omega''\tau_{10}| < 8.5\times10^{-2}$$

or (43)

$$|\Omega''/2\pi| < 2.1 \text{ MHz}.$$

The contribution of $\delta\nu''$ to the experimental shift is then negligible, and we have

$$(\delta\nu)_{\mathrm{expt}} \approx \delta\nu_a' \quad (44)$$

as predicted in Sec. IV B. Then $\Omega'/2\pi \approx -68$ MHz [Eq. (19)].

The small limiting value obtained for $|\Omega''/2\pi|$ is not incompatible with the results of EPR studies of Rb atoms trapped in solid krypton matrices.[12] In these matrices the Rb atom occupies a more or less distorted substitutional site; the Rb-Kr distance for the undistorted site is 4.015 Å, to be compared with $r_m = 4.53$ Å in the Rb-Kr molecule. The experimental observations on the matrix correspond to a value of $\Omega''/2\pi$ *per neighbor*, varying between +39 and −3 MHz.

In view of the smallness of $|\Omega''/2\pi|$ compared with $\bar{\omega}_1/2\pi \sim 6$ MHz in the ^{87}Rb-Kr molecule, and also in view of the experimental uncertainty, we have decided to neglect Ω'' in the computation of the linewidth $\Delta\nu''$ associated with molecular states. Then one may use Eq. (39); the result of the calculation is represented by curve b″ of Fig. 2. The solid curve is the sum of the three calculated contributions: Doppler [Eq. (17), curve d], binary collisions [Eq. (23), curve b′], and molecule formation [Eq. (39), curve b″]. It is seen that the agreement with the experiment is satisfactory. The fact that the data require a relatively large contribution b'' from bound states gives additional evidence for the existence of transient Rb-Kr molecules in the gas mixture.

One should point out as a conclusion that the situation for Rb-Kr molecules where the spin-orbit coupling ($\bar{\omega}_1$) dominates over the change in the hyperfine structure (Ω'') is not necessarily general. As an example, for Rb in argon, preliminary measurements seem to indicate that the reverse situation prevails (i.e., $|\Omega''| \gg \bar{\omega}_1$).[3]

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Practical Approach to the Coupled Equations for Scattering and Rearrangement Collisions*

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The coupled equations of collision theory are examined in the projection-operator formulation of Feshbach. It is shown that the separate treatments of the open and closed channels provide distinct numerical advantages over the conventional methods. As an illustrative example, the phase shift and resonances for the (e, H) system are calculated.

I. INTRODUCTION

In recent years, it has become increasingly clear, with the help of computer facilities, that the coupled-equation approach to collisions can provide reasonably accurate predictions.[1] Substantial efforts have recently been devoted towards further improvements of such predictions by introducing correlation functions in the expansion or by utilizing pseudo-(distorted or polarized) basis states for the expansion of the collision wave function for the formulation of the coupled equations.[2,3] These various approaches have all met with encouraging results and make the coupled-equation approach extremely interesting.

On the other hand, it is well known that the number of coupled equations needing to be solved increases rapidly with the energy of the system because more states should be included in the coupled equations. In the meantime, the number of equations also increases rapidly with the above-mentioned modifications to allow for correlation, polarization, and continuum effects. This then gives rise to serious practical difficulties, even with modern computer facilities. It is, therefore, desirable to investigate whether the number of coupled equations for a given energy region may be kept down; in the meantime, the correlation, polarization, and continuum effects may be accounted for in a natural way. The purpose of the present communication is to show that by treating the closed channels separately from the open channels, as in the Feshbach formulation,[4] such a procedure is provided.

Since the closed-channel wave functions decrease exponentially, and are quadratically integrable, the