Spin relaxation of of rubidium atoms induced by collisional modification of the Rb hyperfine interaction

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Spin relaxation of Rb atoms induced by collisional modification of the hyperfine interaction has been measured for ^{85}Rb and ^{87}Rb in He, Ne, and Ar buffer gases at high magnetic field. The relaxation rates at 40 kG are 0.028 $\text{sec}^{-1}\,\text{Torr}^{-1}$ for ^{85}Rb in He, 0.029 $\text{sec}^{-1}\,\text{Torr}^{-1}$ for ^{85}Rb in Ne, and 0.041 $\text{sec}^{-1}\,\text{Torr}^{-1}$ for ^{85}Rb in Ar. The corresponding relaxation rates for ^{87}Rb are approximately 4.9 times larger, in accord with theory. Cross sections for the binary $\delta a(\vec{S}\cdot\vec{I})$ collisional interaction are estimated to be $\sigma(\delta a(\vec{S}\cdot\vec{I}))(\text{Rb}-\text{He}) = 2.3\times10^{-14}$ cm^2 and $\sigma(\delta a(\vec{S}\cdot\vec{I}))(\text{Rb}-\text{Ne}) = 1.4\times10^{-14}$ cm^2. Anomalous relaxation, R^*, is present in the same degree at 40 kG as at low magnetic field, lending strong support to earlier attributions of R^* to the $\delta a(\vec{S}\cdot\vec{I})$ interaction in Rb-atom–noble-gas-atom van der Waals molecules.

I. INTRODUCTION

The spin density of electrons at the nucleus of a free atom usually is perturbed when the atom collides with a foreign buffer-gas atom or molecule.[1] The resultant modification of the hyperfine interaction, $\delta a(\vec{S}\cdot\vec{I})$, yields the well-known pressure shifts of hyperfine frequencies observed in spin-polarized atomic vapors.[2] Modification of the hyperfine interaction is effective at inducing *relaxation* of electronic- or nuclear-spin polarizations, however, only if the vapor is situated in an external magnetic field strong enough to break the coupling between S and I.[3-6] Since most optical pumping experiments on alkali-metal vapors have been performed in magnetic fields to the order of a 100 G or less, $\delta a(\vec{S}\cdot\vec{I})$ has rightly been ignored as a contributor to relaxation phenomena. The $\delta a(\vec{S}\cdot\vec{I})$ effects discussed in this paper should not be confused with the well-known influence of the hyperfine coupling on electronic and nuclear spin relaxation at low magnetic field: The present considerations involve actual changes of the hyperfine interaction, whereas the latter effects arise from decoupling-recoupling phenomena.

In a previous experiment, relaxation rates for Cs in He and Ne at high magnetic field were found to be substantially larger than those predicted from measurements at low magnetic field.[7] The additional relaxation was attributed to the influence of $\delta a(\vec{S}\cdot\vec{I})$ in sudden binary collisions between Cs atoms and buffer-gas atoms. $\delta a(\vec{S}\cdot\vec{I})$ also has been suggested as the cause of strong anomalous relaxation R^*, observed in Rb and K in He and Ne buffer gases at low magnetic field, thought to arise in the formation of quasibound and bound alkali-metal-atom–noble-gas-atom van der Waals molecules.[8,9] Conclusive proof of the nature of the interaction has not been available, however, in either case.

In the present paper we report relaxation measurements at high magnetic field for ^{85}Rb and ^{87}Rb in He, Ne, and Ar buffer gases. Measurements on Rb are particularly instructive because the only significant difference in relaxation rates for the two Rb isotopes should be that attached to $\delta a(\vec{S}\cdot\vec{I})$ effects. We find that at high magnetic field the $\delta a(\vec{S}\cdot\vec{I})$ interaction in sudden binary collisions indeed makes large contributions to spin relaxation, approximately in the degrees predicted from low-field pressure-shift measurements, and in the strikingly different amounts for ^{85}Rb and ^{87}Rb predicted by theory. We determine the cross sections for the interaction. We also gain important new information on the magnitude of the cross section for normal $\gamma(\vec{S}\cdot\vec{N})$ spin relaxation in sudden binary collisions, and on the characteristics and origin of anomalous relaxation.

II. RELAXATION PROCESSES AND RATE EQUATIONS AT HIGH MAGNETIC FIELD

A. Relaxation processes

We summarize below the various contributions to the relaxation of electronic- and nuclear-spin polarizations, $\langle S_z\rangle$ and $\langle I_z\rangle$, of alkali-metal atoms in high and low magnetic fields. More detailed discussions are available in other papers and review articles.[10,11]

1. Collisional modification of the hyperfine interaction

In the presence of an external magnetic field strong enough to decouple S and I, the modification of the hyperfine interaction of an alkali-metal atom induced in sudden binary collisions with noble-gas atoms yields relaxation of the electronic and nuclear spin. The general equation describing this effect is[3,4,6,8]

$$\langle \dot{S}_z \rangle = -\langle \dot{I}_z \rangle \simeq -R(\delta a(\vec{S}\cdot\vec{I}))\left(\langle S_z\rangle - \frac{S(S+1)}{I(I+1)}\langle I_z\rangle\right). \tag{1}$$

Equation (1) indicates that the $\delta a(\vec{S}\cdot\vec{I})$ interaction does not destroy *total* spin polarization, but rather acts to redistribute polarization between the electronic and nuclear systems.

In general the magnitude of $R(\delta a(\vec{S}\cdot\vec{I}))$ is given by Eq. (2):

$$R(\delta a(\vec{S}\cdot\vec{I})) = \frac{8\pi^2}{3}\,\frac{\langle \delta a\rangle^2 \tau_{\epsilon 1}\tau_{\epsilon 2} I(I+1)\,T_f^{-1}}{1+\Delta W^2\tau_{\epsilon 2}^2}, \tag{2}$$

where T_f^{-1} is the rate at which perturbations (collisions) occur, $\tau_{\epsilon 2}$ is the correlation time for the perturbation, $\tau_{\epsilon 1}$ is the duration of the perturbation, $\langle \delta a\rangle$ is the average shift in the hyperfine constant a, per perturbation, I is the nuclear spin, and ΔW is 2π times the hyperfine frequency. $\tau_{\epsilon 1}$ and $\tau_{\epsilon 2}$ may be written as follows:

$$\tau_{\epsilon 1}^{-1} = \tau_0^{-1} + n_0\sigma_B v_{\rm rel}\, p/p_0, \tag{3a}$$

$$\tau_{\epsilon 2}^{-1} = \tau_0^{-1} + \tau_{\epsilon 2}^{0\,-1} + n_0\sigma_B v_{\rm rel}\, p/p_0, \tag{3b}$$

where τ_0 is the natural lifetime of the complex, $\tau_{\epsilon 2}^0$ is the characteristic correlation time for the interaction in the absence of collisional breakup, and σ_B is the cross section for collisional breakup of complexes.

In the case of sudden binary collisions, T_f^{-1} is simply the average collision rate of alkali atoms with noble-gas atoms,

$$T_f^{-1}(\text{binary}) = n_0\sigma_c v_{\rm rel}\, p/p_0, \tag{4}$$

where n_0 is Loshmidt's number, σ_c is the average cross section for the $\delta a(\vec{S}\cdot\vec{I})$ interaction, $v_{\rm rel}$ is the mean relative velocity of alkali-metal-atoms and noble-gas atoms, p is the buffer-gas pressure, and p_0 is atmospheric pressure. $\langle \delta a\rangle$ can be estimated from low-field measurements of buffer-gas pressure shifts[11]

$$\langle \delta a\rangle \simeq \frac{(\delta\nu)p}{(I+\frac{1}{2})}\,\frac{(n_0\sigma_c v_{\rm rel} p/p_0)^{-1}}{\tau_{\epsilon 2}}, \tag{5}$$

where $\delta\nu$ is the measured pressure shift in Hz/Torr. Assuming that $\delta\nu$, $\tau_{\epsilon 2}$, and σ_c are not themselves dependent upon magnetic field, the rate of relaxation resulting from the $\delta a(\vec{S}\cdot\vec{I})$ interaction in sudden binary collisions of alkali-metal atoms with noble-gas atoms, $R_2(\delta a(\vec{S}\cdot\vec{I}))$, is

$$R_2(\delta a(\vec{S}\cdot\vec{I})) = \frac{8\pi^2}{3}\,\frac{(\delta\nu)^2}{(I+\frac{1}{2})^2}\,(n_0\sigma_c v_{\rm rel}/p_0)^{-1}\,p(I)(I+1), \tag{6}$$

where we have assumed that $\tau_{\epsilon 1} = \tau_{\epsilon 2}$, and $\Delta W\tau_{\epsilon 2} \ll 1$.

In contrast to the relaxation mechanisms described below, the $\delta a(\vec{S}\cdot\vec{I})$ interaction should yield relaxation rates which are markedly different for ^{85}Rb and ^{87}Rb in any particular buffer gas. Noting that the mechanical parameters in Eq. (6) are approximately equal for the two isotopes, and inserting known values for pressure shifts in ^{85}Rb and ^{87}Rb, we obtain

$$\frac{R_2(\delta a(\vec{S}\cdot\vec{I})(^{87}\text{Rb}))}{R_2(\delta a(\vec{S}\cdot\vec{I})(^{85}\text{Rb}))} \simeq \frac{((\delta\nu)^2(I)(I+1)/(I+\frac{1}{2})^2)^{87}}{((\delta\nu)^2(I)(I+1)/(I+\frac{1}{2})^2)^{85}} \simeq 4.9. \tag{7}$$

Equation (7) presents an important discriminant through which relaxation from the $\delta a(\vec{S}\cdot\vec{I})$ interaction can be identified.

If the external magnetic field is not strong enough to decouple S and I, the relaxation rates displayed in Eqs. (2) and (6) are reduced by a multiplicative scale factor $C(\chi)$, where $\chi = \omega_s/\Delta W$ and $\omega_s = 2\pi g_e\mu_B H_0$. For $\omega_s \ll \Delta W$, $C(\chi)$ reduces to $(\omega_s/\Delta W)^2$, thus in low magnetic field $R_2(\delta a(\vec{S}\cdot\vec{I}))$ approaches zero.[4,6]

2. *Anomalous relaxation*

Alkali atoms in He and Ne buffer gases experience an anomalous contribution to relaxation R^*, which has been attributed to the formation of bound and quasibound alkali-metal-atom–noble-gas-atom van der Waals molecules, and in particular to the $\delta a(\vec{S}\cdot\vec{I})$ interaction present in states of such molecules.[8] Equation (2) thus should describe R^*, with T_f^{-1} representing the formation rate of the van der Waals complexes. The nuclear-spin mechanics are the same as those given by Eq. (1).

A major problem with the attribution of R^* to the $\delta a(\vec{S}\cdot\vec{I})$ interaction is the fact that at the magnetic fields in which previous experiments were performed, $\omega_s/\Delta W \ll 1$, and R^* would be expected to be negligible. It has been suggested that an effective magnetic field, much larger than the external magnetic field may exist in the molecular state, thus explaining this discrepancy.[8] Measurements at high magnetic field, where $C(\chi) = 1$, should reflect the full strength of R^*, and thus should provide new information on this mode of relaxation. A fuller discussion of R^* relaxation based on insights gained from the present work is provided in a separate publication.[12]

3. *Spin-orbit relaxation*

The normal cause of spin relaxation in sudden collisions of alkali-metal atoms with noble-gas atoms is the collisionally induced spin-orbit interaction, $\gamma(\vec{S}\cdot\vec{N})$, between $\vec{S}$, the electronic spin of the alkali-metal atom, and $\vec{N}$, the translational angular momentum of the alkali-metal-atom–

noble-gas-atom pair.[13-16] While nuclear-spin mechanics play a crucial role at low magnetic field in determining how the $\gamma(\vec{S}\cdot\vec{N})$ relaxation rate is reflected in relaxation transients, such effects are absent in high fields where S and I are decoupled. As a result, at high field $R_1(\delta(\vec{S}\cdot\vec{N}))$ acts only on $\langle S_z\rangle$, and $\langle I_z\rangle$ is unperturbed. Relaxation rates in all cases can be expressed in terms of a nuclear-spin independent cross section $\sigma(\gamma(\vec{S}\cdot\vec{N}))$: The value of $\sigma(\gamma(\vec{S}\cdot\vec{N}))$ measured at low magnetic field should be equal to that measured at magnetic fields ranging up to at least 100 kG. The $\gamma(\vec{S}\cdot\vec{N})$ relaxation rate due to sudden binary Rb–noble-gas-atom collisions is represented as follows:

$$R_1(\gamma(\vec{S}\cdot\vec{N}))=n_0\sigma(\gamma(\vec{S}\cdot\vec{N}))v_{\rm rel}\,p/p_0\,. \tag{8}$$

The $\gamma(\vec{S}\cdot\vec{N})$ interaction also dominates spin-relaxation processes in van der Waals molecules of alkali-metal atoms and heavy noble-gas atoms.[15] Calculations show that $\gamma(\vec{S}\cdot\vec{N})$ effects should be negligible in complexes containing He or Ne as a partner, however, both at low and high magnetic fields.

4. Relaxation at the walls of the cell

Franzen's approximation, in which relaxation due to diffusion of atoms to the walls of the cell is taken to be described wholly by the first diffusion mode, has been shown to be accurate under the conditions of low polarization encountered in the present experiment.[17-19] We therefore have the following expression for R', the relaxation rate at the walls of the cell:

$$R'=[(\pi/L)^2+(2.405/r)^2]D_0p_0/p\,, \tag{9}$$

where L is the length of the cell, and r is the radius. D_0 is the diffusion coefficient of Rb in the buffer gas at the temperature of operation of the cell. R' acts equally on both $\langle S_z\rangle$ and $\langle I_z\rangle$.

5. Spin-exchange collisions

At low magnetic field, spin-exchange collisions among similar atoms act through the hyperfine interaction to redistribute polarization between the electronic- and nuclear-spin systems. The effect on relaxation transients can be very large.[20-22] At high field, where the coupling between S and I is broken, polarization transfer between $\langle S_z\rangle$ and $\langle I_z\rangle$ is not expected to occur, thus self-spin exchange should not exert any influence on the $\langle S_z\rangle$ relaxation transient. Spin destruction, i.e., destruction of $\langle S_z\rangle$ through collisions of similar atoms, is several orders-of-magnitude smaller than normal spin-exchange rates and plays no role in our experiment.[23]

6. Pumping

At low magnetic field, σ^+ pumping imparts polarization to both the electronic-and nuclear-spin systems, by causing transitions between $|F, m_F\rangle$ sublevels of the ground and excited states, with $\Delta m_F=+1$. At high magnetic field, only the electronic spin system is polarized directly since pumping transitions occur between $|m_J m_I\rangle$ sublevels, with $\Delta m_I=0$. The rate equation for $\langle S_z\rangle$ therefore can contain a pumping term while the $\langle I_z\rangle$ equation does not. Polarization can be transmitted indirectly from $\langle S_z\rangle$ to $\langle I_z\rangle$, however, by a relaxation mechanism such as $\delta a(\vec{S}\cdot\vec{I})$.

B. Rate equations for optical pumping at high magnetic field

The combination of relaxation and pumping mechanisms described in the preceding section lead to Eqs. (10a) and (10b) which summarize the rates of change of $\langle S_z\rangle$ and $\langle I_z\rangle$ for optical pumping and relaxation at high magnetic field

$$\langle\dot{S}_z\rangle=B_1-B_2\langle S_z\rangle+B_3\langle I_z\rangle\,, \tag{10a}$$

$$\langle\dot{I}_z\rangle=-C_2\langle I_z\rangle+C_3\langle S_z\rangle\,. \tag{10b}$$

B_1 is equal to the pumping rate when pumping is present, otherwise B_1 is equal to zero. The equilibrium polarizations reached by a system undergoing simultaneous pumping and relaxation are given by Eqs. (11a) and (11b):

$$\langle I_z\rangle_{\rm eq}=\langle S_z\rangle_{\rm eq}(C_3/C_2) \tag{11a}$$

and

$$\langle S_z\rangle_{\rm eq}=B_1(B_2-B_3C_3/C_2)^{-1}\,. \tag{11b}$$

Equations (11a) and (11b) also describe the initial conditions for the evolution of the spin polarization when the pumping light is shut off and the system allowed to relax in the dark.

The solutions of Eq. (10a) and (10b) are sums of two exponentials. For relaxation in the dark we obtain

$$\langle S_z\rangle=D_+\exp(-Z_+t)+D_-\exp(-Z_-t) \tag{12a}$$

and

$$\langle I_z\rangle=E_+\exp(-Z_+t)+E_-\exp(-Z_-t)\,, \tag{12b}$$

where

$$Z_\pm=\tfrac{1}{2}(B_2+C_2)\pm\tfrac{1}{2}(B_2-C_2)[1+4B_3C_3(B_2-C_2)^{-2}]^{1/2}\,, \tag{13}$$

and the ratio of the amplitudes of the $\langle S_z\rangle$ relaxation transient, (D_+/D_-), is given by Eq. (14):

$$D_+/D_- = [(B_2 - Z_-) - C_3 B_3/C_2] \times [(Z_+ - B_2) + C_3 B_3/C_2]^{-1} . \quad (14)$$

We summarize in Table I the contributions of the various process to relaxation in ^{85}Rb and ^{87}Rb.

Some important practical effects are predicted by Eqs. (10a)–(14).

(i) While there is no direct optical pumping of the nuclear-spin system at high magnetic field, polarization is passed to the nuclear system by $\delta a(\vec{S}\cdot\vec{I})$ relaxation. The coupling of the electronic- and nuclear-spin polarizations through this interaction gives rise to double-exponential relaxation and pumping transients at high field. *The cause of double-exponential transients at high magnetic field is entirely different from the cause of similar double-exponential transients encountered at low magnetic field.* The low-field phenomena derive from collisional decoupling and recoupling of the hyperfine interaction between the electronic and nuclear spin of the alkali-metal atom[24, 25]; the influence of these coupling effects on relaxation is not present in high magnetic fields. The double-exponential behavior at high field arises from collisional modification of the hyperfine interaction, which can induce simultaneous reorientation of $\vec{I}$ and $\vec{S}$.

(ii) The degree to which double-exponential behavior is present at high magnetic fields depends upon the strength of the $\delta a(\vec{S}\cdot\vec{I})$ interaction relative to other interactions. Since for any particular buffer gas $\delta a(\vec{S}\cdot\vec{I})$ is approximately five times stronger in ^{87}Rb than in ^{85}Rb, the double-exponential behavior should be more pronounced in ^{87}Rb than in ^{85}Rb. In the absence of the $\delta a(\vec{S}\cdot\vec{I})$ interaction the pumping and relaxation transients are predicted to be single exponential, with essentially equal rates, for both isotopes.

(iii) The rates Z_+ and Z_- depend upon the individual relaxation rates in a simple way only in special limiting cases. For example, if $R_1 \gg R_2 \gg R'$, $4B_3C_3(B_2 - C_2)^{-2}$ is small, and

$$Z_+ \approx B_2 , \quad (15a)$$

$$Z_- \approx C_2 . \quad (15b)$$

In this limit, $D_+/D_- \sim R_1/R_2 \gg 1$, and the transient approaches a single exponential of rate $Z_+ \approx R_1 + R_2 + R'$.

Conversely, if $R_2 \gg R_1 \gg R'$, $4B_3C_3(B_2 - C_2)^{-2}$ is approximately 0.41 for ^{85}Rb and 1.20 for ^{87}Rb. For ^{87}Rb one obtains

$$Z_+ \simeq 1.25\, B_2 - 0.25\, C_2 , \quad (16a)$$

$$Z_- \simeq -0.25\, B_2 + 1.25\, C_2 , \quad (16b)$$

and, for ^{85}Rb,

$$Z_+ \simeq 1.1\, B_2 - 0.1 C_2 , \quad (17a)$$

$$Z_- \simeq -0.1\, B_2 + 1.1 C_2 . \quad (17b)$$

Once again, $D_+/D_- \sim R_1/R_2$, but now $R_1/R_2 \ll 1$, and the transient approaches a single exponential with the rate $Z_- \approx R'$.

Neither of these limiting cases apply in practice for ^{85}Rb or ^{87}Rb in He or Ne buffer gases at high magnetic field, especially in the pressure range 0–1500 Torr; the value of the term $4B_3C_3(B_2 - C_2)^{-2}$ changes significantly throughout this pressure range. Data therefore must be analyzed iteratively point by point; there is no convenient linear fit of measured relaxation rate to buffer-gas pressure which yields accurate determinations of the relaxation cross sections. Moreover, although R_2 disappears from the exponential rates in both of the limits described above, in the intermediate case where R_2 is comparable to R, R_2 can make significant contributions to Z_+, as we shall see indeed is the case.

TABLE I. Contributions of various processes to relaxation equations, where R' = wall relaxation rate, $R_1 = \gamma(\vec{S}\cdot\vec{N})$ relaxation rate, $R_2 = \delta a(\vec{S}\cdot\vec{I})$ relaxation rate in binary collisions, and R^* = anomalous relaxation rate.

	^{85}Rb ($I=\frac{5}{2}$)	^{87}Rb ($I=\frac{3}{2}$)
B_1	$A/4$	$A/4$
B_2	$R' + R_1 + R_2(85) + R^*(85)$	$R' + R_1 + R_2(87) + R^*(87)$
B_3	$(\frac{3}{35})\lvert R_2(85) + R^*(85)\rvert$	$(\frac{1}{5})\lvert R_2(87) + R^*(87)\rvert$
C_2	$(\frac{3}{35})\lvert R_2(85) + R^*(85)\rvert + R'$	$(\frac{1}{5})\lvert R_2(87) + R^*(87)\rvert + R'$
C_3	$R_2(85) + R^*(85)$	$R_2(87) + R^*(87)$

III. EXPERIMENTAL APPARATUS

The experimental arrangement was similar to that described in Ref. 7. An intense beam of white pumping light was spectrally narrowed by a succession of filters to a width of about 10 Å around the D_1(7947 Å) line of Rb, chopped, reflected vertically, circularly polarized, and passed into the room temperature access bore of a superconducting solenoid containing the experimental cell. A partially filtered unpolarized weak detection beam of white light with equal intensities at the D_1 and D_2 (7800 Å) lines was passed through the cell in the opposite direction. The detection beam then passed through the pumping polarizer, the reflecting filter, and a succession of narrow band D_2 filters, and ultimately was monitored by

an unbiased photodiode connected through a high gain preamplifier to a signal averager.

A major improvement in signal-to-noise ratio was achieved by permitting less stringent rejection of light from the chopped D_1 pumping beam into the D_2 detection channel than that utilized previously, thus allowing a greater pumping intensity; the present D_2/D_1 rejection ratio was of the order of 10^{-4} at line center. Triggering of the signal averager was delayed until the chopper fully blocked the pumping light in order to eliminate the possibility of spurious transients.

The cylindrical experimental cells, interior length 2.5 cm, interior diameter 2.1 cm, were constructed of pyrex tubing, with optically polished pyrex windows. Filling of the cells with a separated isotope of Rb (isotopic purity 98% or better) and buffer gas was done on an all metal and glass bakable ultrahigh vacuum system. Research grade gases were utilized (non-noble gas impurities less than 1 ppm for Ne and He). Pressures higher than 600 Torr were obtained by filling the cell with gas from the room temperature manifold while the cell itself was immersed in liquid N_2, sealing off, and then allowing the cell to warm back to ambient temperature. Each data point for each isotope at each buffer-gas pressure thus required a separately prepared cell.

Cells were mounted individually into a thermostatically controlled holder which utilized "thermocoax" as the heating element. The holder was then placed at the magnet center of the bore of the room temperature access magnet Dewar. Depending upon relaxation rate, between 2048 and 8192 sweeps of the experimental signal were averaged in each measurement.

IV. EXPERIMENTAL RESULTS AND ANALYSES

In Fig. 1 we reproduce relaxation transients measured for ^{85}Rb and ^{87}Rb in equal pressures of buffer gas, 547 Torr of He at 50°C. The magnetic field was 40 kG. The smooth curves are computer fits to the 256 channel experimental data. The ^{85}Rb data are fit extremely well by a single exponential. Calculations utilizing the experimentally determined relaxation parameters confirm that for this case Eqs. (12) and (13) yield a transient dominated by Z_+, with $D_+/D_- \approx 4$, $Z_+ = 37.3\ \text{sec}^{-1}$, and $Z_- = 4.1\ \text{sec}^{-1}$. The ^{87}Rb data, however, are strongly double exponential, and have been so fit. Calculations confirm that in this case $D_+/D_- \simeq 0.37$, $Z_+ \simeq 101\ \text{sec}^{-1}$, and $Z_- \simeq 5.4\ \text{sec}^{-1}$; the relative amplitude of the "slow" component D_-, is more than ten times greater in ^{87}Rb than in ^{85}Rb and cannot be neglected. The considerable difference between the ^{85}Rb and ^{87}Rb transients is due in part to the more pronounced nuclear-spin dependence for $I = \frac{3}{2}$ as compared to that for $I = \frac{5}{2}$ (see Table I), and in part to the greater strength of the $\delta a(\vec{S}\cdot\vec{I})$ interaction for ^{87}Rb as compared to that for ^{85}Rb. Z_+, the "fast" relaxation rate, receives full contributions from R_1, R_2, and R^*, and thus is the experimental observable of primary interest in the present experiment.

While a low cell temperature is preferred in order to reduce differential pumping effects caused by strong absorption of the pumping or detection beams as they traverse the cell, signal-to-noise considerations favor a higher vapor pressure and hence a higher cell temperature. Measurements of ^{85}Rb relaxation transients over the range from 37.5 °C–50 °C showed no appreciable change with temperature. About half of our data, primarily that for the relatively long time constants available in ^{85}Rb, was taken at 37.5 °C. The remainder, primarily that associated with high relaxation rates, was taken at 50 °C. All data reported below are presented in terms of the equivalent measurements at 37.5 °C, that is, a relaxation rate measured at 50 °C is divided by 1.02 and is displayed at the pressure the cell would have at 37.5 °C.[27]

A. Relaxation of ^{85}Rb and ^{87}Rb in He and Ne

In Figs. 2 and 3 we display the results of measurements of Z_+ for ^{85}Rb and ^{87}Rb in He and Ne at 37.5 °C and 40 kG. Each point is an average of three or more separate measurements. The solid curves represent the relaxation rates which are predicted from the diffusion coefficients and $\gamma(\vec{S}\cdot\vec{N})$ cross sections previously measured at low magnetic field, neglecting contributions from R_2 and R^* relaxation. Under that circumstance, the relaxation rates for ^{85}Rb and ^{87}Rb are predicted to be equal. Examination of the data, however, shows striking differences between the ^{85}Rb and ^{87}Rb relaxation rates in He and Ne, and substantial differences of each of these rates from the low-field predictions. The differences are due primarily to the enhancement of $\delta a(\vec{S}\cdot\vec{I})$ relaxation at high magnetic field and to the significantly greater value of $R_2(\delta a(\vec{S}\cdot\vec{I}))$ for ^{87}Rb expected at any particular buffer-gas pressure compared to that expected for ^{85}Rb. These measurements constitute the first conclusive demonstration of the influence of $\delta a(\vec{S}\cdot\vec{I})$ relaxation in sudden binary collisions.

We have extracted values of $R_2(\delta a(\vec{S}\cdot\vec{I}))$ and R^* from the data in Figs. 2 and 3 subject to the following assumptions and restrictions. All calculations utilize Eqs. (10a)–(14) previously discussed.

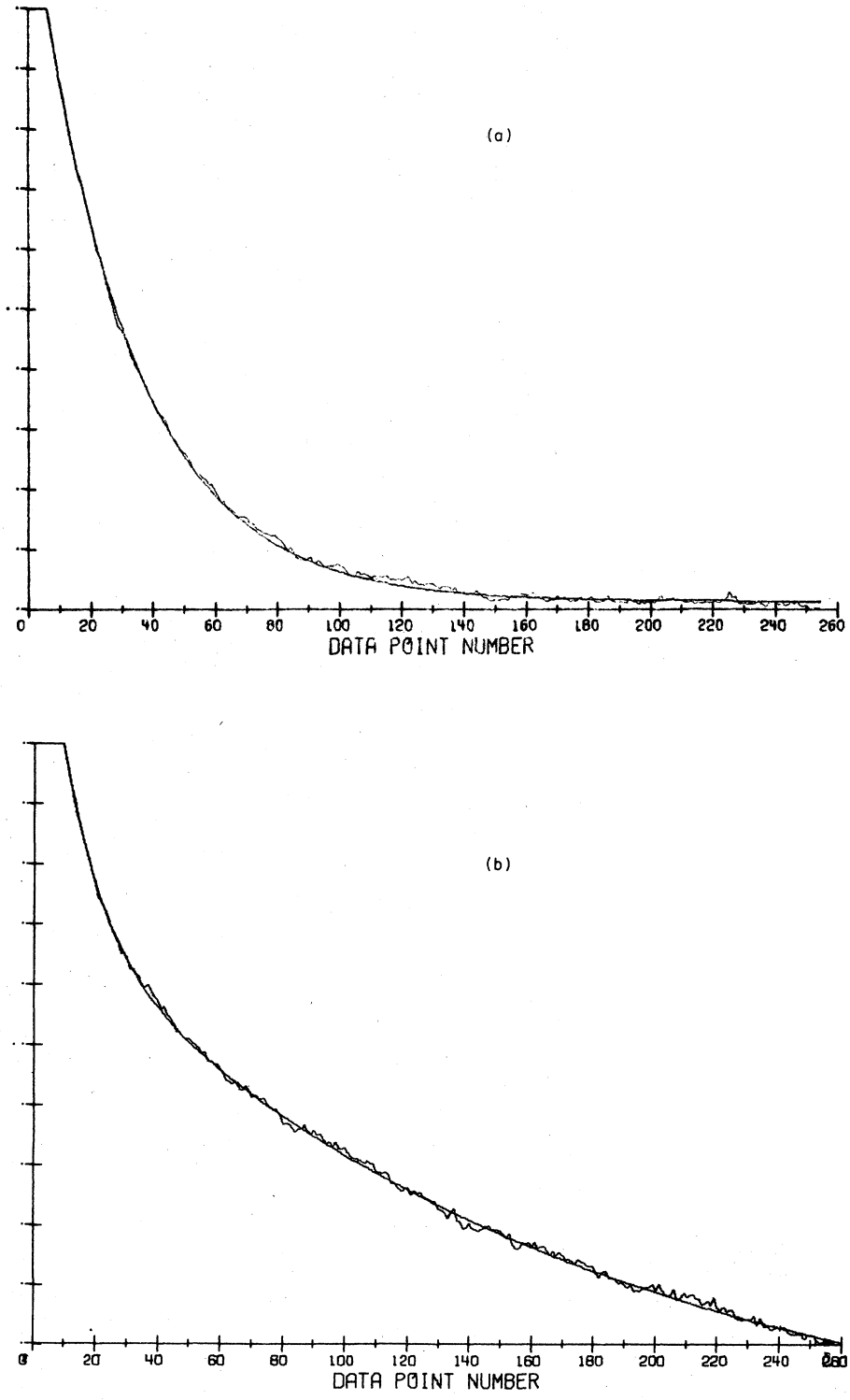

FIG. 1. (a) Measured relaxation transients and computer fits at 40 kG for ^{85}Rb in He, and (b) ^{87}Rb in He. The He pressure was 547 Torr in both cases. The ^{85}Rb transient is approximately single exponential; the ^{87}Rb transient is strongly double exponential. The horizontal axis is 200 m sec full scale. See text.

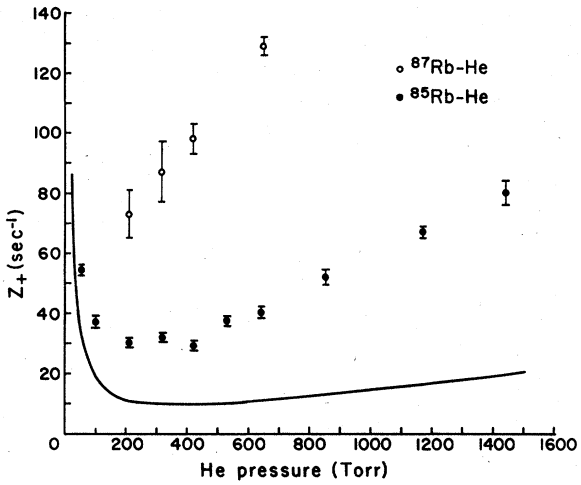

FIG. 2. Measurements of the "fast" relaxation rate Z_+, for ^{85}Rb and ^{87}Rb in He. Uncertainties are ±1 standard deviation. The solid curve represents an extrapolation from low-field measurements ignoring the $\delta a(\vec{S}\cdot\vec{I})$ interaction.

(1). The wall relaxation rate, R', is calculated from the parameters in Ref. 8, corrected for temperature assuming $D = D_0(T/273)^{3/2}$. For Rb in He, Ne, and Ar in the present experiment we have

$$R' = (1760/p), (980/p), (712/p),$$

respectively, at 37.5 °C.

(2). The $\gamma(\vec{S}\cdot\vec{N})$ relaxation rate is calculated from the nuclear-spin independent cross sections measured at low magnetic field. For Rb in He and Ne in the present experiment we have

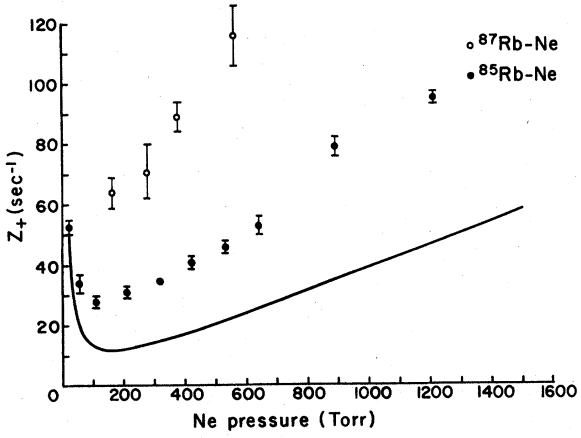

FIG. 3. Measurements of the fast relaxation rate Z_+, for ^{85}Rb and ^{87}Rb in Ne. Uncertainties are ±1 standard deviation. The solid curve represents an extrapolation from low-field measurements ignoring the $\delta a(\vec{S}\cdot\vec{I})$ interaction.

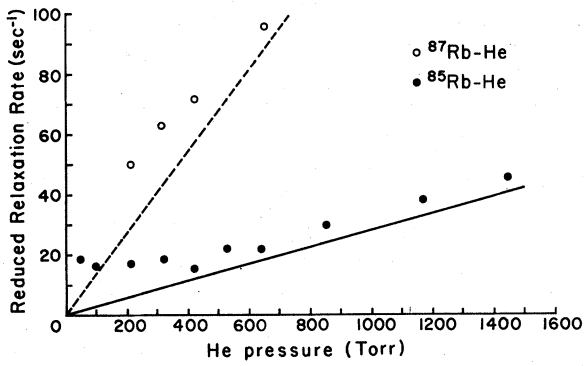

FIG. 4. "Reduced data" for ^{85}Rb and ^{87}Rb relaxation in He at 40 kG. See text.

$$R_1(\gamma(\vec{S}\cdot\vec{N})) = (.021p), (.038p),$$

respectively, at 37.5 °C.

(3). The $\delta a(\vec{S}\cdot\vec{I})$ relaxation rate required to be added to $R_1 + R'$ to reproduce Z_+ at each data point is calculated. The values of these "reduced relaxation rates," assumed to be the sum of R_2 $(\delta a(\vec{S}\cdot\vec{I}))$ and R^*, are displayed in Figs. 4 and 5.

The cross section for $\gamma(\vec{S}\cdot\vec{N})$ relaxation of Rb in He reported in Ref. 8 was 3.1×10^{-24} cm^2, corresponding to a relaxation rate of $0.013p$ expected in the present experiment. The data of Ref. 8 extend only to 500 Torr, however, in which pressure range anomalous relaxation is about an order-of-magnitude greater than binary relaxation. A small relative error in the estimation of anomalous relaxation, therefore, can lead to a large relative uncertainty in $\sigma(\gamma(\vec{S}\cdot\vec{N}))$. Stimulated by results from the present experiment, we measured relaxation rates of Rb in He at low magnetic field at pressures as high as 1500 Torr. Combining these data with those in Ref. 8, we find that the best value of $\sigma(\gamma(\vec{S}\cdot\vec{N}))$ to be 5.1×10^{-24} cm^2, corresponding to a relaxa-

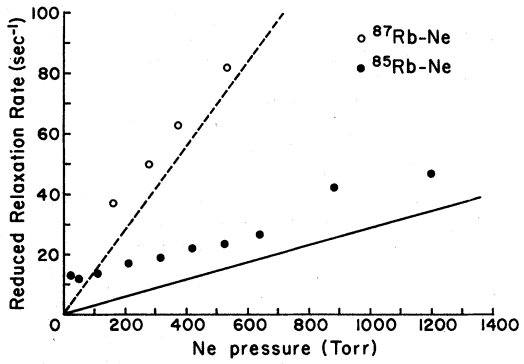

FIG. 5. Reduced data for ^{85}Rb and ^{87}Rb relaxation in Ne at 40 kG. See text.

tion rate of $0.021p$ in the present experiment. We have used this value in the present analysis. We also have made low-field measurements of the relaxation of Rb in Ne up to 1500 Torr, and in that case have found full agreement with the earlier reported cross section, 1.9×10^{-24} cm^2. Further discussion of all of these measurements will appear in a separate publication.

Separation of the reduced relaxation rates into $R_2(\delta a(\vec{S}\cdot\vec{I}))$ and R^* components requires additional assumptions. We note that at high buffer-gas pressure $\tau_{\epsilon1}^{-2}$ and $\tau_{\epsilon2}^{-2}$ in Eqs. (3a) and (3b) go as p^2. If molecular formation occurs via two-body collisions (quasibound molecular states), then T_f^{-1} is proportional to p, and R^* in Eq. (2) passes through a maximum and approaches zero at high p. If molecular formation occurs primarily via three-body collisions (bound and quasibound states), then T_f^{-1} is proportional to p^2, and R^* approaches a constant value at high p. $R_2(\delta a(\vec{S}\cdot\vec{I}))$, on the other hand, must be proportional to p. $R_2(\delta a(\vec{S}\cdot\vec{I}))$ therefore should be represented by a straight line through the origin, passing either through the reduced data at the highest pressures or parallel to it. Since the most reasonable expectation is that molecular formation at high pressure occurs primarily via three-body collisions, we have chosen to make the latter fit as shown in Figs. 4 and 5.

The fact that relaxation rates in ^{87}Rb are considerably greater than for ^{85}Rb made it impractical for us to make measurements in ^{87}Rb at pressures above about 600 Torr. Since R^* is appreciable in ^{85}Rb in the pressure range 0—600 Torr, and since R^* in ^{87}Rb should be at least equal to that in ^{85}Rb, a linear fit to the ^{87}Rb data in this particular pressure range is inappropriate. Instead, we show with the dashed lines in Figs. 4 and 5 the $R_2(\delta a(\vec{S}\cdot\vec{I}))$ relaxation rates that are predicted for ^{87}Rb from the ^{85}Rb results: that is, $R_2(\delta a(\vec{S}\cdot\vec{I}))(87)=4.9R_2(\delta a(\vec{S}\cdot\vec{I}))(85)$, and demonstrate compatibility between projection and measurement.

From the fits to the reduced data in Figs. 4 and 5 we obtain the $R_2(\delta a(\vec{S}\cdot\vec{I}))$ relaxation rates listed in Table II. Taking values of $\delta\nu$ as measured by Vanier *et al.*,[26] we find through Eq. (6) the values of the effective cross section, σ_c, for the $\delta a(\vec{S}\cdot\vec{I})$ interaction which we also list in Table II. While we measured striking differences in relaxation rates for Rb in He and Ne at low and high magnetic fields, we measured no significant changes in these relaxation rates throughout the range of magnetic fields from 20 kG to 95 kG.

The results displayed in Figs. 4 and 5 yield new information on the nature of anomalous relaxation. The primary problem with the attribution of anomalous relaxation to the $\delta a(\vec{S}\cdot\vec{I})$ interaction in Rb-atom—noble-gas-atom van der Waals molecules has been the fact that although estimated formation rates and $\delta a(\vec{S}\cdot\vec{I})$ shifts yield relaxation rates that are consistent with measured values of R^*, at low magnetic field these relaxation rates should be reduced by the factor $C(\chi)$, making them negligibly small. Ad hoc assumptions such as the existence of a strong effective magnetic field in the molecular state are required.[8] Figures 4 and 5 show that the high-field values of R^* in fact are comparable to the low-field values, suggesting that $C(\chi)\approx1$ even at low magnetic field, lending strong support to the effective-field argument. We shall explore this and related points in a separate paper.

TABLE II. Rates for $\delta a(\vec{S}\cdot\vec{I})$ relaxation in binary collision of ^{85}Rb with He, Ne, and Ar measured at high magnetic field. $\delta\nu$ is the pressure shift measured at low magnetic field, and $\sigma(\delta a(\vec{S}\cdot\vec{I}))$ is the cross section for the $\delta a(\vec{S}\cdot\vec{I})$ interaction, estimated from Eq. (6).

	$R_2(\delta a(\vec{S}\cdot\vec{I}))$ sec^{-1} Torr^{-1}	$\delta\nu$[a] (Hz/Torr)	$\sigma(\delta a(\vec{S}\cdot\vec{I}))$ (cm^2)
Rb-He	0.028	328	2.3×10^{-14}
Rb-Ne	0.029	179	1.4×10^{-14}
Rb-Ar	0.041	−24	

[a]Reference 26.

B. Relaxation of ^{85}Rb and ^{87}Rb in Ar

We also have measured high-field relaxation rates for ^{85}Rb and ^{87}Rb in Ar, over Ar pressures ranging from 20—150 Torr. Since the hyperfine pressure shift for Rb in Ar is small, and the $\gamma(\vec{S}\cdot\vec{N})$ binary relaxation rate is relatively large, one expects relatively little difference between relaxation rates at low and high magnetic fields. Furthermore, since $R_1>R_2\gg R'$, the first limiting approximation discussed in Eqs. (15a) and (15b) applies, and we can present reduced data in the following simple form:

$$R(\text{reduced})=Z_+-R'\simeq R+R_2+R^*. \tag{18}$$

The inaccuracy introduced through the use of Eq. (18) is less than 4% in the present case.

We display reduced data for ^{85}Rb and ^{87}Rb in Ar in Fig. 6. As was the case for Rb in He and Ne, we have made linear fits from the origin parallel to the data points measured at highest pressure, both for ^{85}Rb and ^{87}Rb. These fits should determine R_1+R_2 for each isotope, with the "excess" of the reduced relaxation rate (that remaining above the linear fit) representing R^*.

The evaluated slopes of the reduced relaxation rates, $\Delta(R_1+R_2)/\Delta p$, for ^{85}Rb and ^{87}Rb in Ar are

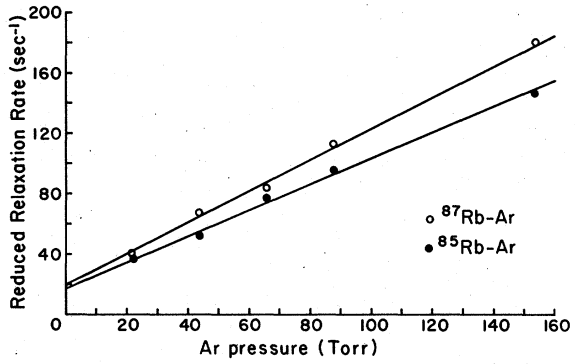

FIG. 6. Reduced data for ^{85}Rb and ^{87}Rb relaxation in Ar at 40 kG. See text.

given in Table III. The conditions that $R_2(87) = 4.9R_2(85)$ and $R_1(87) = R_1(85)$ allow the determination of the individual R and R_2 contributions; these are also listed in Table III. From the value of 0.083 determined for $\Delta R_1/\Delta p$, we find that $\sigma(\delta(\vec{S}\cdot\vec{N})(\text{Rb-Ar})) = 540\times10^{-24}$ cm^2, about 17% smaller than the value previously determine at low magnetic field. We discuss this point further below.

The necessity to make assumptions about the pressure dependence of R^* in order to extract cross sections for $\gamma(\vec{S}\cdot\vec{N})$ and $\delta a(\vec{S}\cdot\vec{I})$ relaxation in sudden binary collisions results in a degree of added uncertainty in these cross sections. While the 17% difference between the high- and low-field measurements of $\sigma(\gamma(\vec{S}\cdot\vec{N}))$ for Rb-Ar therefore could fall within the combined uncertainties of the two experiments, there are reasons to believe that this discrepancy may instead have physical significance. If two-body quasimolecular collisions make a significant contribution to $\gamma(\vec{S}\cdot\vec{N})$ relaxation at low magnetic field, such a contribution would be difficult to distinguish from relaxation arising from sudden binary collisions; up to pressures of several hundred Torr both could have a linear dependence on p. At 40 kG, however, the electronic Zeeman frequency should be significantly greater than the inverse of the correlation time for the quasimolecular interaction. In such a case the measured relaxation rate would reflect only the influence of sudden binary collisions; the difference between low- and high-field relaxation rates would reflect contributions from quasimolecular $\gamma(\vec{S}\cdot\vec{N})$ interactions.

TABLE III. Relaxation rates in Rb-Ar. See text.

	$\Delta(R_1+R_2)/\Delta p$ sec^{-1} Torr^{-1}	$\Delta R_1/\Delta p$ sec^{-1} Torr^{-1}	$\Delta R_2/\Delta p$ sec^{-1} Torr^{-1}
^{85}Rb-Ar	0.87	0.83	0.041
^{87}Rb-Ar	1.03	0.83	0.200

Some evidence supporting the above idea may lie in a comparison of the relaxation measurements of Vanier, Simard, and Boulanger (VSB)[26] with those of Franz and Volk (FV).[8] VSB measured the relaxation of $\langle\vec{S}\cdot\vec{I}\rangle$ of Rb in N_2 and Ar, while FV measured the relaxation of $\langle S_z\rangle$ of Rb in the same two buffer gasses. All measurements were made at low magnetic field. For Rb in N_2 the two experiments yielded almost identical cross sections, 80×10^{-24} cm^2 and 83×10^{-24} cm^2, respectively. For Rb in Ar, however, the $\langle\vec{S}\cdot\vec{I}\rangle$ experiment yielded a significantly smaller cross section than that yielded by the $\langle S_z\rangle$ experiment, 490×10^{-24} cm^2 compared to 630×10^{-24} cm^2. The discrepancy between these two sets of measurements has not been explained. VSB's evaluation of relaxation data neglected R^* effects; FV estimated that if these were appropriately considered, the $\gamma(\vec{S}\cdot\vec{N})$ cross section evaluated from VSB's data would be about 10% higher than that reported, or about 540×10^{-24} cm^2. This value is in striking agreement with the high-field Rb-Ar cross section evaluated in the present experiment.

All of these results can be reconciled if the lifetimes of the postulated quasibound complexes were longer than the Rb hyperfine period, but shorter than the characteristic collisional breakup time. In that case, quasibound binary effects could exert a strong influence on $\langle S_z\rangle$ relaxation at low magnetic field, but a weak influence on $\langle\vec{S}\cdot\vec{I}\rangle$ relaxation and, as explained above, a weak influence on $\langle S_z\rangle$ relaxation at high magnetic field.

We have shown earlier that for Rb in He and Ne, the $\delta a(\vec{S}\cdot\vec{I})$ interaction competes with the $\gamma(\vec{S}\cdot\vec{N})$ interaction as the dominant mode of relaxation, making ^{85}Rb and ^{87}Rb relaxation rates significantly different in these gases at high magnetic field. For Rb in Ar, on the other hand, contributions from the $\gamma(\vec{S}\cdot\vec{I})$, and differences between ^{85}Rb and ^{87}Rb relaxation rates are relatively small. An intriguing point, however, is that although *relatively* small, the $\delta a(\vec{S}\cdot\vec{I})$ relaxation rates for Rb and Ar in fact are far larger than those predicted by Eq. (5). It is known that the pressure shift measured for Rb in Ar is small because of averaging of positive contributions from short range encounters with negative contributions from long-range interactions. Relaxation, on the other hand, can be induced by either shift; we suggest that the averaging to a near zero effect does not occur in the case of relaxation. Indeed, it seems possible that correlation of relaxation data with pressure-shift

data could yield new information on the separation of long- and short-range $\delta a(\vec{S}\cdot\vec{I})$ effects.

V. SUMMARY

Collisional modification of the hyperfine interaction yields spin-relaxation rates at high magnetic field which are comparable to those from other modes of relaxation. The $\delta a(\vec{S}\cdot\vec{I})$ relaxation rates measured for ^{85}Rb and ^{87}Rb in various buffer gases differ by a factor proportional to the square of the ratio of the low-field hyperfine pressure shifts, as predicted by theory. The high-field measurements confirm the existence of anomalous relaxation previously observed at low magnetic field and attributed to spin relaxation induced by the $\delta a(\vec{S}\cdot\vec{I})$ interaction in alkali–noble-gas van der Waals molecules. In a subsequent publication we shall show how correlations of the present high-field measurements with previous low-field measurements yield important new information on the nature of anomalous relaxation.

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[1]See, for example, S. Ray, G. Das, P. Maldonado, and A. Wahl, Phys. Rev. A 2, 2196 (1970); R. R. Freeman, D. E. Pritchard, and D. Kleppner, Phys. Rev. A 13, 907 (1976); R. R. Freeman, E. M. Mattison, D. E. Pritchard, and D. Kleppner, J. Chem. Phys. 64, 1194 (1976).

[2]See, for example, P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Lett. 1, 311 (1958); C. W. Beer and R. A. Bernheim, Phys. Rev. A 13, 1052 (1976).

[3]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

[4]M. A. Bouchiat, Ph.D. thesis, University of Paris, 1964 (unpublished); J. Phys. (Paris) 24, 370 (1963); 24, 611 (1963).

[5]F. Hartmann and F. Hartmann-Boutron, Phys. Rev. A 2, 1885 (1970).

[6]C. Volk, Ph.D. thesis, Indiana University, 1977 (unpublished).

[7]T. R. Marshall, R. Boggy, and F. A. Franz, Phys. Rev. A 16, 618 (1977).

[8]F. A. Franz and C. Volk, Phys. Rev. Lett. 35, 1704 (1975); Phys. Rev. A 14, 1711 (1976); Phys. Rev. A 18, 599 (1978); and unpublished.

[9]van der Waals molecules also play a crucial role in polarization exchange between Rb atoms and with gas nuclei. See, C. H. Volk, T. M. Kwon, and J. G. Mark, Phys. Rev. A 21, 1549 (1980).

[10]L. C. Balling, *Advances in Quantum Electronics*, edited by D. W. Goodwin (Academic, New York, 1975), Vol. 3.

[11]W. Happer, Rev. Mod. Phys. 44, 169 (1972).

[12]F. A. Franz and A. Sieradzan (unpublished).

[13]R. A. Bernheim, J. Chem. Phys. 36, 135 (1962).

[14]R. M. Herman, Phys. Rev. 136, A1576 (1964).

[15]C. C. Bouchiat, M. A. Bouchiat, and L. C. L. Pottier, Phys. Rev. 181, 144 (1969).

[16]M. A. Bouchiat and J. Brossel, Phys. Rev. 147, 41 (1966).

[17]W. Franzen, Phys. Rev. 105, 850 (1959).

[18]P. Minguzzi, F. Strumia, and P. Violino, Nuovo Cimento 46, 145 (1966).

[19]F. A. Franz, Phys. Rev. A 6, 1921 (1972).

[20]H. Gibbs, Phys. Rev. 139, A1374 (1965).

[21]H. Gibbs and R. J. Hall, Phys. Rev. 153, 132 (1967).

[22]H. Gibbs, thesis, University of California at Berkeley, 1965 (unpublished).

[23]N. D. Bhaskar, J. Pietras, J. Comparo, W. Happer, and J. Liran, Phys. Rev. Lett. 44, 930 (1980).

[24]F. Masnou Seeuws and M. A. Bouchiat, J. Phys. 28, 406 (1967).

[25]F. A. Franz and C. E. Sooriamoorthi, Phys. Rev. A 8, 2390 (1973); 10, 126 (1974).

[26]J. Vanier, J.-F. Simard, and J.-S. Boulanger, Phys. Rev. A 9, 1031 (1974).

[27]Considering the temperature dependences of n_0, $v_{\rm rel}$, p, and D_0, it is easy to show, for a *sealed* cell in which the total amount of gas remains constant, that $z_+(T_1)/z_+(T_2)\simeq(T_1/T_2)^{1/2}$.