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Spin relaxation of rubidium atoms in sudden and quasimolecular collisions with light-noble-gas atoms*

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Spin relaxation of optically pumped Rb^{85} and Rb^{87} atoms colliding with light-noble-gas atoms is shown to be strongly influenced by an anomalous relaxation process which we attribute to the formation and destruction of bound and quasibound Van der Waals molecules. The anomalous relaxation rate has been measured and analyzed in Ne, complementing an earlier study in He. Relative rates of formation of complexes in two- and three-body collisions have been determined. The correlation time for the quasimolecular interaction in Rb-Ne has been found to be $6.7\times10^{-10}p^{-1}$ sec, where p is the Ne pressure in Torr. Nuclear-spin-independent cross sections for the relaxation of $\langle S_z\rangle$ in sudden binary collisions of Rb atoms with noble-gas atoms have been measured to be (units of 10^{-24} cm^2): $\sigma(\text{Rb-He})=3.1, \sigma(\text{Rb-Ne})=19, \sigma(\text{Rb-Ar})=630, \sigma(\text{Rb-N}_2)=83$. Relaxation in sudden binary collisions is shown to follow the theoretically expected nuclear spin dynamics: two relaxation rates in the ratios 8:1 for Rb^{87} and 18:1 for Rb^{85} have been measured. Diffusion coefficients of Rb in the various buffer gases have been measured to be (units of cm^2/sec, at 305°K): $D_0(\text{Rb-He})=0.42, D_0(\text{Rb-Ne})=0.235, D_0(\text{Rb-Ar})=0.16, D_0(\text{Rb-N}_2)=0.16$. Nuclear-spin-independent cross sections for the relaxation of $\langle J_z\rangle$ in the $5\,^2P_{1/2}$ state of Rb have been measured to be 3.4×10^{-16} cm^2 for Rb-He, and 5.9×10^{-16} cm^2 for Rb-Ne. Anomalies, disagreements, and puzzles occurring in earlier measurements of ground-state relaxation in Rb are shown to be largely resolved when considered in the light of the new results.

I. INTRODUCTION

Even though many of the intricacies of spin relaxation in optically pumped alkali-metal–noble-gas systems are well understood, these systems continue to provide surprises which can be exploited in intriguing ways.[1] Recently, it has been shown that the electronic spin-relaxation rate of Rb in He appears to be affected by the formation and destruction of quasibound Rb-He molecules.[2] The rate of relaxation attributed to molecular formation is as much as an order of magnitude greater than that arising from ordinary binary collisions, just in the range of He pressures where optical pumping experiments often have been performed. This discovery both adds to our understanding of the causes of alkali-metal spin relaxation in He, and provides the opportunity for the study of the Rb-He quasibound molecule, an entity which exists in an otherwise unobservable concentration of 10^3 to 10^4 cm^3 in a typical experimental cell. An optical pumping experiment has yielded the relative rates of formation of Rb-He quasibound molecules in two- and three-body collisions, the cross sections for their collisional breakup, and their lifetime against spontaneous dissociation.

If quasimolecular interactions play such a significant role in the spin relaxation of Rb in He, as well as in the already well-known case of Rb in Kr,[3-6] then surely they should play a role also in the relaxation of Rb in the remaining noble gases. We show in the present paper that this appears to be the case. We report the results of measurements of spin-relaxation rates of Rb^{85} and Rb^{87} in Ne, Ar, and N_2 buffer gases, as well as an extension of previous measurements in He. We determine the nuclear-spin independent cross sections for electron spin relaxation in sudden binary collisions of Rb with atoms of each of these gases, together with the Rb-buffer-gas mutual-diffusion coefficients. For He and Ne, where anomalous effects are largest relative to normal relaxation processes, we extract from experimental data those portions of the relaxation rates which can be attributed to the formation of bound and quasibound molecules. From this information we evaluate the relative rates of formation of Rb-Ne molecular complexes in two- and three-body collisions, and the correlation time of the collisional interaction. We study the influence of the hyperfine interaction on spin relaxation in quasibound molecules, and find anomalous behavior which is not yet fully understood. On the other hand, we show that the nuclear spin dynamics generally expected to result from sudden binary collisions do in fact obtain, and that relaxation via quasimolecular formation merges into this scheme at high buffer-gas pressures. We utilize our ground-state pumping transients to investigate the effects of collisional relaxation within the Rb $5\,^2P_{1/2}$ excited state. Finally, we correlate our results and analyses with other studies on comparable systems, and show that long-standing anomalies in relaxation measurements are resolved when effects due to quasimolecular formation are taken into account.

II. PUMPING EQUATIONS FOR Rb^{85} AND Rb^{87} IN THE WEAK-PUMPING LIMIT

Our experiment involves normal $\sigma^{+}D_1$ optical pumping of separated isotopes of Rb^{85} and Rb^{87}, with the observables of interest being the electronic spin polarization $\langle S_z\rangle_g$ and the nuclear spin polarization $\langle I_z\rangle_g$ of the Rb atomic ground state.[7] In this section we review the forms expected for the optical pumping transients of these two isotopes. The customary definitions apply:

$$\langle S_z\rangle_g=\sum_i n_i\langle S_z\rangle_{gi}\Big/\sum_i n_i \tag{1a}$$

and

$$\langle I_z\rangle_g=\sum_i n_i\langle I_z\rangle_{gi}\Big/\sum_i n_i, \tag{1b}$$

where n_i is the occupation probability of the ith $|F,m_F\rangle$ sublevel of the $^2S_{1/2}$ ground state, $\langle S_z\rangle_{gi}$ and $\langle I_z\rangle_{gi}$ are the expectation values of the electronic and nuclear spins in the ith sublevel, and we assume

$$\sum_i n_i\approx 1. \tag{2}$$

In some experiments, the observable $\langle\vec{S}\cdot\vec{I}\rangle_g$ is of interest:

$$\langle\vec{S}\cdot\vec{I}\rangle_g=\sum_i n_i\langle\vec{S}\cdot\vec{I}\rangle_{gi}\Big/\sum n_i. \tag{3}$$

The magnitudes of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ depend upon the relative rates of pumping from the ground state, collisional relaxation within the excited state, self-spin exchange within the ground state, and various processes of collisional relaxation within the ground state. Since all of these processes have been discussed in detail in other publications, we shall review only the essential features here.

A. Relaxation in sudden binary collisions

A collision of an alkali-metal atom with a buffer-gas atom subjects the electron spin of the alkali-metal atom to a randomly oriented transient local magnetic field, an action which may induce relaxation of the electronic spin. Since the direct collisional interaction is several orders of magnitude stronger on the electronic spin than on the nuclear spin, nuclear reorientation occurs mainly through the hyperfine interaction of the nucleus with the reoriented electron. In the case of alkali-metal atoms, the hyperfine period is far longer than the duration of a typical binary collision, hence little nuclear reorientation occurs during the collision itself. In effect, a collision suddenly throws an atom from a well-defined $|F,m_F\rangle$ sublevel into a superposition of $|F',m_{F'}\rangle$ sublevels, with $\langle I_z\rangle$ conserved: subsequent nuclear reorientation occurs in the time between relaxing collisions. Appropriate calculations based on this picture lead to the "electron-randomization" model of spin relaxation first introduced by Bender.[9] A more-general treatment for arbitrary correlation time of the collisional interaction has been developed by Bouchiat and co-workers, who have derived the following equations for the rates of change of $\langle S_z\rangle_g$, $\langle I_z\rangle_g$, and $\langle\vec{S}\cdot\vec{I}\rangle_g$, of alkali-metal atoms subject to random static magnetic perturbations[9-11]

$$\langle\dot{S}_z\rangle_g=-C\left(\frac{j(\omega_F)-j(\Delta W)}{(2I+1)^2}+j(\Delta W)\right)\langle S_z\rangle_g$$

$$+\frac{2C}{(2I+1)^2}\,j(\Delta W)\langle I_z\rangle_g, \tag{4a}$$

$$\langle\dot{I}_z\rangle_g=\frac{-C}{(2I+1)}\,[j(\omega_F)+j(\Delta W)]\,\langle I_z\rangle_g, \tag{4b}$$

$$d\langle\vec{S}\cdot\vec{I}\rangle_g/dt=-Cj(\Delta W)\,\langle\vec{S}\cdot\vec{I}\rangle_g, \tag{4c}$$

where $j(\omega_F)$ and $j(\Delta W)$ are the intensities of the spectral density function for the perturbation at the Zeeman frequency ($\Delta F=0$, $\Delta m_F=\pm 1$), and at the hyperfine frequency ($\Delta F=\pm 1$), respectively. C represents the equivalent low-magnetic-field relaxation rate for a nuclear-spin zero atom. For $j(\omega_F)=j(\Delta W)$, the equations reduce to those for "electron randomization," with R, the nuclear-spin-independent rate for the relaxation of $\langle S_z\rangle_g$ being equal to $Cj(\omega_F)=Cj(\Delta W)$. In that case we have Eqs. (5a)–(5c) and (6a)–(6c):

$$\left.\begin{aligned}
&\langle\dot{S}_z\rangle_g=-R\langle S_z\rangle_g+\tfrac{1}{18}R\langle I_z\rangle_g, &&(5a)\\
&\langle\dot{I}_z\rangle_g=-\tfrac{1}{18}R\langle I_z\rangle_g, &&(5b)\\
&d\langle\vec{S}\cdot\vec{I}\rangle_g/dt=-R\langle\vec{S}\cdot\vec{I}\rangle_g; &&(5c)
\end{aligned}\right\}\quad(Rb^{85})$$

$$\left.\begin{aligned}
&\langle\dot{S}_z\rangle_g=-R\langle S_z\rangle_g+\tfrac{1}{8}R\langle I_z\rangle_g, &&(6a)\\
&\langle\dot{I}_z\rangle_g=-\tfrac{1}{8}R\langle I_z\rangle_g, &&(6b)\\
&d\langle\vec{S}\cdot\vec{I}\rangle_g/dt=-R\langle\vec{S}\cdot\vec{I}\rangle_g. &&(6c)
\end{aligned}\right\}\quad(Rb^{87})$$

The explicit form of R is given by

$$R=n_0\sigma v_{\mathrm{rel}}\,p/p_0, \tag{7}$$

where σ is the nuclear-spin-independent cross section for electron spin relaxation in the $^2S_{1/2}$ state, v_{rel} is the mean relative velocity of Rb atoms and buffer-gas atoms, n_0 is Loschmidt's number (2.69×10^{19} cm^{-3}) corrected to the temperature of the experimental cell, p is the buffer-gas pressure, and p_0 is atmospheric pressure.

Equations analogous to Eqs. (5a)–(5c) and (6a)–(6c) also apply to the collisional relaxation of $\langle J_z\rangle$ in the $^2P_{1/2}$ excited state. The application of these equations to the description of collisional relaxation within the excited state, and its effect upon the repopulation rates of $\langle S_z \rangle_g$ and $\langle I_z \rangle_g$, has been discussed in detail in Ref. 12. The repopulation rates, whose explicit forms will be given in a later section, are found to depend only upon τ, the natural lifetime of the excited state, and upon Γ_1, the nuclear-spin-independent rate for the collisional relaxation of $\langle J_z \rangle$, where

$$\Gamma_1 = n_0 \sigma_1 v_{\text{rel}} p/p_0 \tag{8}$$

and σ_1 is the nuclear-spin-independent cross section for the collisional relaxation of $\langle J_z \rangle$.

B. Relaxation in quasimolecular collisions

The simplest physically reasonable model that can be used to describe the effect of quasimolecular collisions is to assume that during such a collision the Rb electronic spin is subjected to a randomly oriented additional magnetic field h, which we assume lasts for an average time τ_c, the correlation time for the collisional interaction. We include in this term the effective magnetic interactions during the creation and destruction of the molecule, plus the perturbation which exists during the lifetime of the molecule. One then calculates the effective relaxation rate for an ensemble of atoms subject to such randomly occurring perturbations. The calculation closely parallels an example provided by Slichter.[13] Bouchiat, Bouchiat, and Pottier have provided an equivalent derivation.[4] One obtains

$$R^* = A^* \tau_c^2 (1 + \omega_0^2 \tau_c^2)^{-1}, \tag{9}$$

where ω_0 is the resonant frequency for the electron spin polarization, and A is a factor directly proportional to the rate of formation of complexes. In our case we expect A^* to be of the form

$$A^* = Bp + Cp^2, \tag{10}$$

where Bp is proportional to the formation rate of quasibound complexes in two body collisions, and Cp^2 is proportional to the formation rate of quasibound plus bound complexes in three body collisions.

In the case of Rb-He, using Mahan's formulation[14] and Baylis's potential parameters[15] we have calculated that there should be one bound state (twofold degenerate), and one quasibound state (sixfold degenerate). This result has been confirmed independently by Kiehl.[16] In this very special case, then, Rb-He collisions are more apt to form molecules which are quasibound than those which are truly bound. Moreover, since there is only one quasibound state, a unique lifetime against dissociation by tunneling through the centrifugal barrier can be attributed to it. In the more-general case in other buffer gases we expect a division of about $\frac{2}{3}$ states bound, $\frac{1}{3}$ quasibound, with a wide distribution of dissociative lifetimes for the quasibound states.[17]

As an initial approximation we assume that Eqs. (4a)–(4c) should describe the nuclear-spin effects in relaxation via formation and destruction of bound and quasibound Rb-light–noble-gas Van der Waals molecules. We define R^* as the analog, for quasimolecular collisions, of the relaxation rate R, which applies to sudden binary collisions. There is no expectation that $j^*(\Delta W)$ and $j^*(\omega_F)$ should be equal in the quasimolecular case. The relative magnitudes of these two quantities will depend upon the correlation time for the quasimolecular interaction, probably upon the effective lifetime of the quasibound complex. Since this lifetime depends upon the collisional breakup rate, we anticipate that both the absolute and relative magnitudes of $j^*(\Delta W)$ and $j^*(\omega_F)$ will depend to some degree upon buffer-gas pressure, in contradistinction to the case for simple binary collisions. These parameters also will be influenced by the lifetime of the complex against spontaneous dissociation.

C. Relaxation due to electronic spin exchange

Spin exchange would play no role in changing the magnitude of $\langle S_z \rangle_g$ if the nuclear spin were zero. In practice, however, the presence of the hyperfine interaction allows spin exchange to influence observed relaxation rates through an interconversion of nuclear and electronic spin polarizations. Spin exchange phenomena have been studied by many persons, only a few of whom we reference here.[18-20] A particularly useful formulation was presented by Gibbs, who showed that in the limit of very small polarization, the case in the present experiment, the following equations apply[21]:

$$\begin{aligned} \langle \dot{S}_z \rangle_g = -\langle \dot{I}_z \rangle_g = {} & -R_s \langle S_z \rangle_g [+2I(2I-1)2I + 2I(2I-1)2 + (2I+2)(2I+3)2I]\,[3(2I+1)^3]^{-1} \\ & + R_s \langle I_z \rangle_g [-2I(2I-1) + (2I+2)(2I+3)][3(2I+1)^3]^{-1}, \end{aligned} \tag{11}$$

where

$$R_s = n_0 \sigma_s v_{\text{Rb-Rb}} p_{\text{Rb}}/p_0. \tag{12}$$

n_0 is Loschmidt's number corrected to the temperature of the cell, σ_s is the nuclear-spin-independent cross section for Rb electronic spin exchange, $v_{\text{Rb-Rb}}$ is the mean relative velocity of Rb atoms, and p_{Rb} is the Rb partial pressure.

D. Relaxation at the walls of the cell

A rigorous treatment of the effects of relaxation at the walls of the optical-pumping cell requires both an adequate description of the effect of the hyperfine interaction on a single relaxation event, and the solution of an appropriate diffusion equation. Franzen originally suggested that a possible model for relaxation might be to assume that every $|F, m_F\rangle$ sublevel of the alkali-metal atom ground state can be reached with equal probability in a single relaxation event.[22] While this approximation of "uniform relaxation" does not describe the effects of collisions of alkali-metal atoms with buffer-gas atoms, nor with coated cell walls, it appears to describe reasonably well the effect of collisions of alkali-metal atoms with bare Pyrex cell walls, the experimental situation in the present work. Franzen also proposed the approximation that only the lowest-order term of the full series solution to the diffusion equation be retained. It since has been shown that when the spin polarization is very low, that is, when pumping rates are small compared to relaxation rates, Franzen's approximation is accurate to a degree better than customary experimental uncentainties.[23,24] The assumption of the uniform model for wall relaxation, taken with the retention of only the lowest order term of the solution of the diffusion equation, leads to the following relaxation equations for $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$, due to wall collisions alone:

$$\langle \dot{S}_z\rangle_g = -R'\langle S_z\rangle_g, \tag{13a}$$

$$\langle \dot{I}_z\rangle_g = -R'\langle I_z\rangle_g, \tag{13b}$$

where, for a cylindrical cell,

$$R' = [(\pi/L)^2 + (2.405/r)^2] D_0 p_0/p. \tag{14}$$

L and r are the length and radius of the experimental cell, D_0 is the diffusion coefficient of Rb in the buffer gas at the temperature of the cell, p_0 is atmospheric pressure, and p is the pressure of the buffer gas. An equation of the same form as Eqs. (13a) and (13b) also describes the relaxation of $\langle \vec{S}\cdot\vec{I}\rangle_g$.

E. Generalized pumping equations

If the pumping rate is small compared to the relaxation rate of $\langle S_z\rangle_g$, then the contributions of all pumping and relaxation processes mentioned so far can be combined in equations of the following form[25,26]:

$$\langle \dot{S}_z\rangle_g = B_1 - B_2\langle S_z\rangle_g + B_3\langle I_z\rangle_g, \tag{15a}$$

$$\langle \dot{I}_z\rangle_g = C_1 - C_2\langle I_z\rangle_g + C_3\langle S_z\rangle_g. \tag{15b}$$

The explicit forms of the B_i and C_i for Rb^{85} and Rb^{87} are as follows:

Rb^{85} $(I = \frac{5}{2})$:

$$B_1 = A[\tfrac{19}{324} + \tfrac{1}{486}(43\Gamma_1\tau - 101)(1+\Gamma_1\tau)^{-1}(18+\Gamma_1\tau)^{-1}], \tag{16a}$$

$$B_2 = \tfrac{1}{3}A + R + R' + \tfrac{35}{54}R_s + R^*, \tag{16b}$$

$$B_3 = \tfrac{1}{18}(R + R_s + R^*), \tag{16c}$$

$$C_1 = A[\tfrac{35}{324} + \tfrac{875}{486}(18+\Gamma_1\tau)^{-1}], \tag{16d}$$

$$C_2 = \tfrac{1}{3}A + \tfrac{1}{18}R + R' + \tfrac{1}{18}Rs + \tfrac{1}{18}R^*, \tag{16e}$$

$$C_3 = \tfrac{35}{54}R_s; \tag{16f}$$

Rb^{87} $(I = \frac{3}{2})$:

$$B_1 = A[\tfrac{1}{16} + \tfrac{1}{36}(3\Gamma_1\tau - 1)(1+\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1}], \tag{17a}$$

$$B_2 = \tfrac{1}{3}A + R + R' + \tfrac{5}{8}Rs + R^*, \tag{17b}$$

$$B_3 = \tfrac{1}{8}(R + R_s + R^*), \tag{17c}$$

$$C_1 = A[\tfrac{5}{48} + \tfrac{25}{36}(8+\Gamma_1\tau)^{-1}], \tag{17d}$$

$$C_2 = \tfrac{1}{3}A + \tfrac{1}{8}R + R' + \tfrac{1}{8}R_s + \tfrac{1}{8}R^*, \tag{17e}$$

$$C_3 = \tfrac{5}{8}R_s, \tag{17f}$$

where A is the pumping rate, and we tentatively have assumed that $j^*(\omega_F) = j^*(\Delta W)$ for R^*. The other parameters are defined in earlier sections.

Assuming the initial conditions that $\langle S_z\rangle_g(t=0) = \langle I_z\rangle_g(t=0) = 0$, Eqs. (15a) and (15b) yield the following solution for $\langle S_z\rangle_g$:

$$\langle S_z\rangle_g = D_1(1 - e^{-Z_1 t}) + D_2(1 - e^{-Z_2 t}). \tag{18}$$

The rate constants Z_1 and Z_2 are given by

$$Z_1 = \tfrac{1}{2}\{[B_2 + C_2] - [B_2 - C_2] \times [1 + 4B_3C_3(B_2 - C_2)^{-2}]^{1/2}\}, \tag{19a}$$

$$Z_2 = \tfrac{1}{2}\{[B_2 + C_2] + [B_2 - C_2] \times [1 + 4B_3C_3(B_2 - C_2)^{-2}]^{1/2}\}. \tag{19b}$$

Under the conditions of our experiment (relatively low spin-exchange rate), Eqs. (20a) and (20b) approximate the rate constants to an accuracy of better than 97%:

$$Z_1 = C_2 - B_3C_3(B_2 - C_2)^{-1}, \tag{20a}$$

$$Z_2 = B_2 + B_3C_3(B_2 - C_2)^{-1}. \tag{20b}$$

The exact solution for the ratio of the amplitudes of the two exponential terms in Eq. (18) is

$$\frac{D_1}{D_2} = \frac{-B_3C_1Z_2 - B_1C_2Z_2 + B_1B_2C_2 - B_1B_3C_3}{-B_1B_2C_2 + B_1B_3C_3 + B_3C_1Z_1 + B_1C_2Z_1}\ . \tag{21}$$

For spin-exchange rates of the order of the $\langle S_z\rangle$ relaxation rate or less, Eq. (21) reduces to Eq. (22):

$$\frac{D_1}{D_2}=\frac{-B_2B_3C_1(B_2-C_2)-B_3C_3(B_3C_1+B_1B_2)}{(B_2-C_2)(-B_1B_2C_2+B_1B_3C_3+B_3C_1C_2+B_1C_2^2)-B_3C_3(B_3C_1+B_1C_2)}. \tag{22}$$

There are several points relating to Eqs. (18)-(21) which bear special emphasis.

(a) While Eq. (11) conserves total polarization ($\langle S_z\rangle_g+\langle I_z\rangle_g$), it conserves $\langle S_z\rangle_g$ alone only under special circumstances. As a result, the $\langle S_z\rangle_g$ transient usually is affected by spin exchange: although spin exchange has virtually no effect on the "slow" rate constant Z_1, it can have a strong effect both on the "fast" rate constant Z_2, and on the ratio of amplitudes D_1/D_2.

(b) At very low buffer-gas pressures, the wall relaxation rate R' becomes dominant in B_2 and C_2. In that case Z_1 and Z_2 approach common values, and the $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ transients effectively become single exponentials, with equal time constants. We exploit this behavior in the present paper to measure the diffusion coefficients of Rb in the various buffer gases.

(c) When the spin-exchange rate is very high, the $\langle S_z\rangle_g$ transient becomes single exponential. In that case Eq. (19a) yields the same result as that predicted in the limit of the "spin temperature equilibrium," namely, that the nuclear-spin-independent rate for electron randomization relaxation is "slowed" by the factor 0.079 for Rb^{85}, and by the factor 0.167 for Rb^{87}.[1,27] At very-low buffer-gas pressures, where uniform relaxation rather than electron randomization relaxation is dominant, the single exponential relaxation rate is determined by the wall relaxation rate, unchanged from its normal value.

III. MEASUREMENTS OF $\langle S_z\rangle_g$ PUMPING TRANSIENTS

We made our measurements using a relatively standard optical-pumping rig adapted for Rb. A full description appears in Ref. 26. The optical-pumping-cell–gas handling system was all metal and glass, and was baked out prior to use. After bakeout (vacuum about 10^{-7} Torr), dry N_2 was admitted to the system, calcium shavings and the chloride of the appropriate separated isotope were added to a side arm of the optical pumping cell, and the system was pumped out. After several hours the Rb was distilled into the optical pumping cell, and the side arm was drawn off. During the experiment the cell (internal length 7.4 cm, internal radius 3.45 cm) was electrically heated by a noninductive element, and was thermostatically maintained at a temperature of 305.0 °C ± 0.1 °C.

The pumping light was filtered white light obtained from a current-regulated tungsten projector lamp. The light entering the optical-pumping cell was filtered to a band width of 50 Å at 7950 Å. After passing through the cell, the light was further filtered to a bandwidth of 3 Å before impinging on the photodetector.

Optical-pumping transients were measured by observing the response of the system after saturating the ground-state Zeeman resonance. Signal-averaging techniques were used, with generally between 10^{10} to 10^{15} sweeps of the signal being made. The appropriate theoretical function, either one or two exponentials, was then fit to the averaged transient. At least five such measurements were made at each buffer-gas pressure reported.

Since we shall utilize the Rb-He and Rb-Ne experimental data for a rather wide variety of purposes, we record it first in tabular form in Tables I–IV. Large values of D_1/D_2 reflect a relatively small amplitude of the "fast" exponential in the pumping transient. The result is that Z_2 generally is less well determined for Rb^{87} than for Rb^{85}. We therefore have based most of our primary analyses on the Rb^{85} data.

IV. ANALYSES AND DISCUSSION

A. Nuclear-spin-independent cross sections for the relaxation of $\langle S_z\rangle_g$ in sudden binary collisions of Rb atoms with noble-gas atoms

The nuclear-spin-independent cross sections for the collisional relaxation of $\langle S_z\rangle_g$ in binary collisions of Rb atoms with noble-gas atoms (σ) can be determined from measurements of the difference between the two relaxation rates, Z_1 and Z_2, which make up the $\langle S_z\rangle_g$ pumping transient. From Eqs. (20a) and (20b) we obtain

$$(Z_2-Z_1)=B_2-C_2+2B_3C_3(B_2-C_2)^{-1}. \tag{23}$$

For all $R>R_s$, the term $2B_3C_3(B_2-C_2)^{-1}$ varies

TABLE I. Parameters evaluated from fits of Eq. (18) to measured optical-pumping transients. The error estimates are one standard deviation of at least five measurements. Z_1 and Z_2 are the rate constants and D_1/D_2 is the ratio of the amplitudes of the two exponentials. Pumping transient parameters for Rb^{85} in He.

He p (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2
527	1.89 ± 0.04	21.7 ± 1.5	2.51 ± 0.15
409	1.98 ± 0.03	20.9 ± 0.7	2.40 ± 0.03
270	2.17 ± 0.13	18.9 ± 1.5	2.21 ± 0.10
164	2.59 ± 0.17	18.5 ± 1.5	1.97 ± 0.13
100	3.66 ± 0.26	22.6 ± 1.5	2.24 ± 0.28
60.0	4.69 ± 0.10	22.4 ± 1.9	1.88 ± 0.23
35.1	6.65 ± 0.57	22.6 ± 1.3	1.35 ± 0.17

TABLE II. Parameters evaluated from fits of Eq. (18) to measured optical-pumping transients. The error estimates are one standard deviation of at least five measurements. Z_1 and Z_2 are the rate constants and D_1/D_2 is the ratio of the amplitudes of the two exponentials. Pumping transient parameters for Rb^{87} in He.

He p (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2
391	2.58 ± 0.06	20.2 ± 1.9	4.74 ± 0.22
390	2.68 ± 0.06	21.9 ± 1.6	4.99 ± 0.43
125	3.15 ± 0.08	20.6 ± 1.1	5.20 ± 0.50
60	4.40 ± 0.33	20.4 ± 3.2	4.02 ± 0.86
30	7.54 ± 0.17	20.7 ± 1.0	2.89 ± 0.33

from approximately $0.05R_s$ to $0.04R_s$ for Rb^{85}, and from approximately $0.11R_s$ to $0.09R_s$ for Rb^{87}. It therefore is both relatively small and constant at high buffer-gas pressures. R^*, as we shall see, also is essentially constant at high buffer-gas pressures. We therefore may take the slopes of $(Z_2 - Z_1)$ vs p at high buffer-gas pressure to be given by Eqs. (24a) and (24b) the cumulative uncertainty of which we estimate to be less than 5%:

$$\frac{d(Z_2 - Z_1)}{dp} = \tfrac{17}{18} n_0 \sigma v_{\rm rel}/p_0 \quad (I = \tfrac{5}{2}) \tag{24a}$$

$$= \tfrac{7}{8} n_0 \sigma v_{\rm rel}/p_0 \quad (I = \tfrac{3}{2}). \tag{24b}$$

In Figs. 1, 2, and 3 we plot the measured values of $(Z_2 - Z_1)$ for Rb^{85} and Rb^{87} in Ne, Ar, and N_2. The solid line in each case is a least-mean-squares linear fit to the Rb^{85} data. Insertion of the evaluated slope into Eq. (24b) provides a determination of σ. We summarize the results in Table V along with the results for Rb-He from Ref. 2.

We also display $(Z_2 - Z_1)$ data for Rb^{87} in Figs. 1–3. The dashed lines are projections of the Rb^{87} results which would be predicted on the basis of the determination of σ from the Rb^{85} data, and on the assumption that the same degree of anomalous relaxation exists for Rb^{87} as for Rb^{85}. The cross sections evaluated for the relaxation of $\langle S_z \rangle_g$ indeed are seen to be nuclear spin independent: the correlations between measurements for Rb^{85} and Rb^{87} are excellent.

Many previous measurements of alkali spin relaxation have been analyzed on the mistaken assumption that the "uniform" model of relaxation correctly described relaxation in alkali-atom–

TABLE III. Parameters evaluated from fits of Eq. (18) to measured optical-pumping transients. The error estimates are one standard deviation of at least five measurements. Z_1 and Z_2 are the rate constants and D_1/D_2 is the ratio of the amplitudes of the two exponentials. Pumping transient parameters for Rb^{85} in Ne.

Ne p (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2
535	3.20 ± 0.15	37.1 ± 0.2	2.29 ± 0.08
400	2.72 ± 0.07	32.0 ± 0.6	2.52 ± 0.01
300	2.49 ± 0.08	28.0 ± 2.0	2.66 ± 0.13
200	2.31 ± 0.08	24.5 ± 2.4	2.88 ± 0.19
100	2.26 ± 0.02	20.4 ± 0.7	2.82 ± 0.04
65.0	2.73 ± 0.08	21.3 ± 0.9	3.07 ± 0.20
40.4	3.80 ± 0.06	23.7 ± 0.5	2.97 ± 0.14
25.1	5.25 ± 0.45	27.9 ± 5.0	2.59 ± 0.69
18.0	7.36 ± 0.59	26.3 ± 3.6	2.49 ± 0.82
13.0	9.92 ± 0.53	27.1 ± 1.7	2.17 ± 0.07

TABLE IV. Parameters evaluated from fits of Eq. (18) to measured optical-pumping transients. The error estimates are one standard deviation of at least five measurements. Z_1 and Z_2 are the rate constants and D_1/D_2 is the ratio of the amplitudes of the two exponentials. Pumping transient parameters for Rb^{87} in Ne.

Ne p (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2
485	4.42 ± 0.28	37.6 ± 6.0	3.87 ± 0.46
484	4.58 ± 0.27	35.8 ± 4.3	3.79 ± 0.36
349	3.76 ± 0.24	29.3 ± 2.7	4.18 ± 0.37
175	2.91 ± 0.05	25.1 ± 1.7	5.66 ± 0.30
120	2.79 ± 0.05	22.1 ± 2.7	6.57 ± 0.26

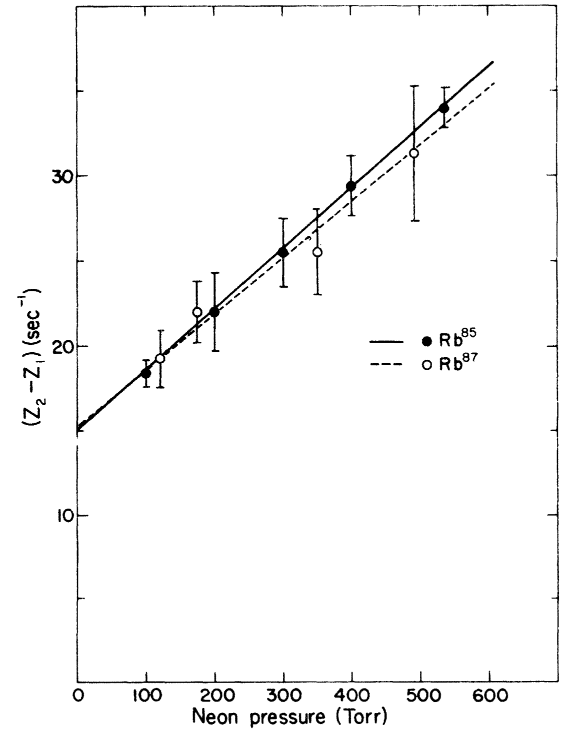

FIG. 1. Plots of measured differences of rate constants $(Z_2 - Z_1)$ from double exponential fits to optical-pumping transients of Rb^{85} and Rb^{87} in high pressures of Ne at 32 °C.

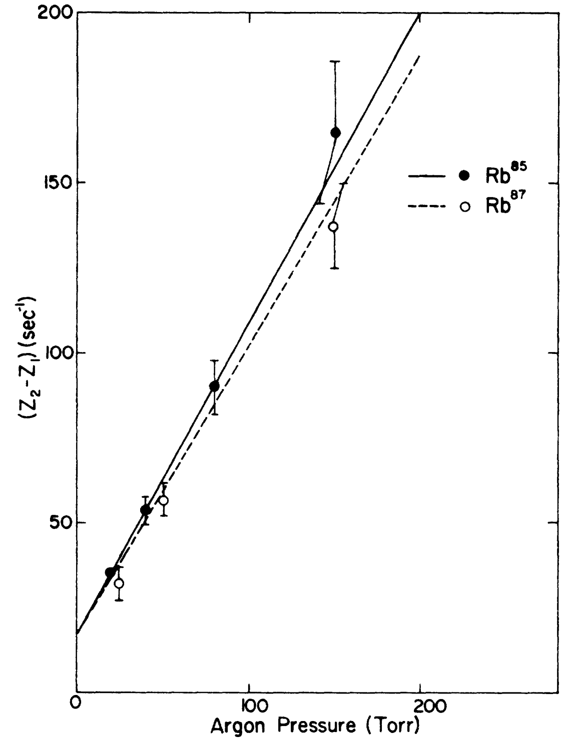

FIG. 2. Plots of measured differences of rate constants (Z_2-Z_1) from double-exponential fits to optical-pumping transients of Rb^{85} and Rb^{87} in high pressures of Ar at 32 °C.

buffer-gas-atom collisions, and in ignorance of important contributions of anomalous relaxation due to molecular formation. As a result, many previously reported cross sections are seriously in error, some by an order of magnitude or more. Toward the end of this paper we shall show that the true cross sections listed in Table V, taken with the diffusion coefficients listed in Sec. IV B and the measured degrees of anomalous relaxation, in fact explain most all previously published relevant data.

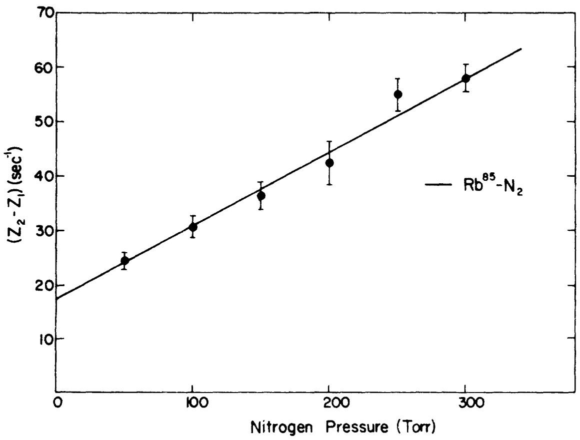

FIG. 3. Plot of measured differences of rate constants (Z_2-Z_1) from double exponential fits to optical-pumping transients of Rb^{85} in high pressures of N_2 at 32 °C.

B. Diffusion coefficients of Rb in He, Ne, Ar, and N_2

At very-low buffer-gas pressures relaxation arises primarily from collisions of pumped atoms with the walls of the experimental cell. The term R' then dominates in Eqs. (13b) and (14b), and Z_1 and Z_2 approach values which differ mainly in different contributions by spin exchange. Under these circumstances the $\langle S_z\rangle_g$ transient effectively becomes a single exponential. It has been shown that when $Z_2 \lesssim 1.5 Z_1$, the following equations approximate the true double exponential to an accuracy of better than 97%:

$$\langle S_z\rangle_g = D_3(1-\exp(-Z_3 t)), \tag{25a}$$

where

$$D_3 = D_1 + D_2 \tag{25b}$$

and

$$Z_3 = (D_1 Z_1 + D_2 Z_2)(D_1 + D_2)^{-1}, \tag{25c}$$

and D_1, Z_1, D_2, and Z_2 remain as defined by Eqs. (16a), (16b), (17a), and (17b).

The situation can be complicated by the presence of contributions to relaxation rates from the formation of Van der Waals molecules.[3-5] Two effects are possible. Either one, if not properly accounted for, can lead to spuriously high determinations of the diffusion coefficient. The first case is that studied by Bouchiat, Brossel, and co-workers, where Rb relaxation via molecular formation at low Kr pressures proceeds essentially according to Eqs. (4a) and (4b), with $j^*(\Delta W) = 0$. This effect, if present, makes a greater contribution to Rb^{87} than to Rb^{85} due to the $(2I+1)^{-2}$ factor in Eqs. (4a) and (4b). The second case is where the formation of bound or quasibound molecular

TABLE V. Slopes and intercepts of least-squares linear fits to data in Figs. 1–3 and in Ref. 2. The evaluated nuclear-spin-independent cross sections for the collisional relaxation of $\langle S_z\rangle_g$ are listed in column 3.

	$d(Z_2-Z_1)/dp$ (sec Torr)$^{-1}$	$(Z_2-Z_1)(p=0)$ (sec^{-1})	$\sigma(S_z)_g$ (10^{-24}cm^2)
He	0.01208	14.0	3.1
Ne	0.0355	15.0	19
Ar	0.9146	17.0	630
N_2	0.1372	17.3	83

complexes yields an appreciable rate of relaxation R^* at the hyperfine frequency $[j^*(\Delta W) \neq 0]$. In this case one expects a greater contribution of R^* to Rb^{85} than to Rb^{87} due to the smaller hyperfine separation of Rb^{85}, that is, $\omega_0^2(\mathrm{Rb}^{85}) < \omega_0^2(\mathrm{Rb}^{87})$ in Eq. (9).

The data presented in Figs. 4 and 5 are obtained from single exponential fits to pumping transients of Rb^{85} and Rb^{87} in low pressures of Ne and Ar. Comparison of the Rb^{85} and Rb^{87} results show molecular-relaxation effects to be relatively small, but far from negligible, at these pressures. The fact that $Z_3(\mathrm{Rb}^{85})$ is generally greater than $Z_3(\mathrm{Rb}^{87})$ indicates the presence of R^* relaxation at the hyperfine frequency. To determine the diffusion coefficients, we fit Eq. (25c) to the Rb^{87} data, which was least affected by R^*, allowing D_0 to be the only variable parameter. The resultant fits are represented by the solid lines in Figs. 4 and 5. In the case of N_2, deexcitation from the Rb excited state occurs via quenching as well as via spontaneous emission. Since the relative probabilities for quenching transitions between Rb Zeeman sublevels are unknown, D_1 and D_2 cannot be calculated, and Eq. (25c) cannot be used in the determination of D_0. For N_2, therefore, we have fit the expression $Z_3 \approx \frac{1}{2}(Z_1 + Z_2)$ to the data. Application of this less-accurate approximation to the other noble gases would change evaluated values of D_0 by less than 5%. We summarize the determinations of D_0 for Rb in He, Ne, Ar, and N_2 in Table VI.

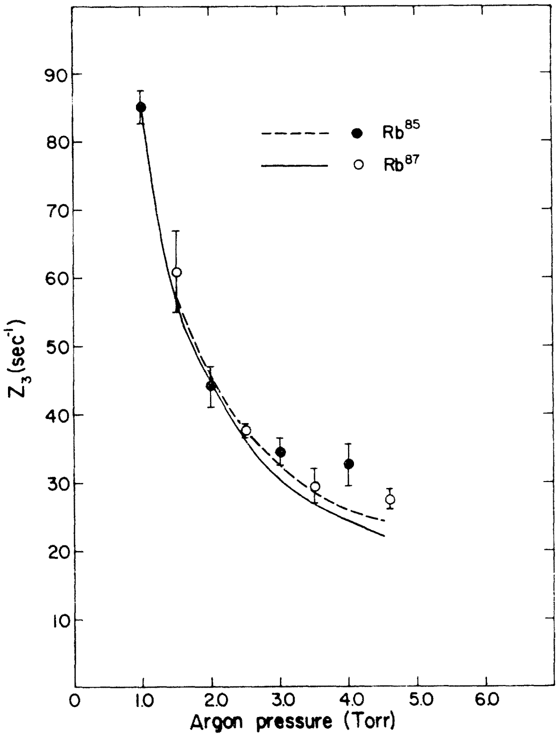

FIG. 5. Fit of Eq. (25) to measured effective single-exponential rate constants of optical-pumping transients of Rb^{87} in low pressures of Ar at 32 °C. The evaluated diffusion coefficient is $D_0(\mathrm{Rb\text{-}Ar}) = 0.16$. The Rb^{85} data falls above that of Rb^{87} due to the presence of quasi-molecular interactions, as discussed in the text.

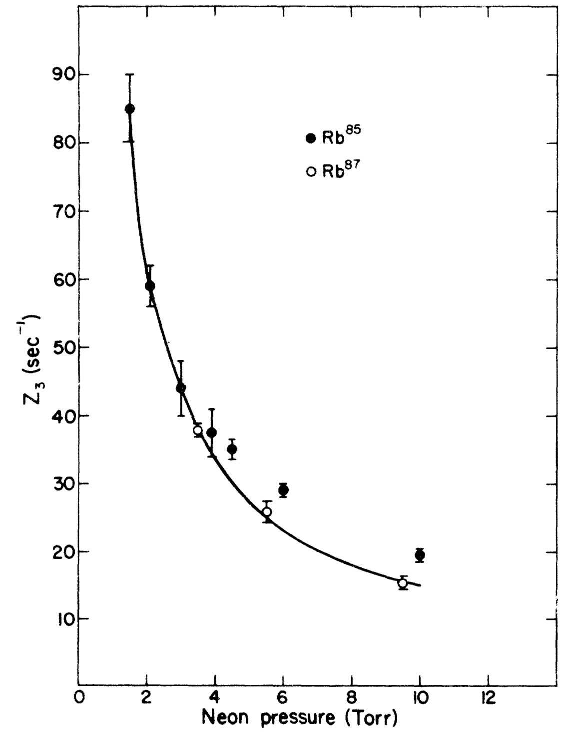

FIG. 4. Fit of Eq. (25) to measured effective single-exponential rate constants of optical-pumping transients of Rb^{87} in low pressures of Ne at 32 °C. The evaluated diffusion coefficient is $D_0(\mathrm{Rb\text{-}Ne}) = 0.235$. The Rb^{85} data falls above that of Rb^{87} due to the presence of quasi-molecular interactions, as discussed in the text.

TABLE VI. Diffusion coefficients (at $p = 1$ atm) for Rb in various buffer gases evaluated at 32 °C, and extrapolated to 0 °C assuming a $T^{3/2}$ dependence.

	D_0 (32 °C) (cm^{2}sec^{-1})	D_0 (273 °K) (cm^{2}sec^{-1})
Rb-He	0.42	0.36
Rb-Ne	0.235	0.20
Rb-Ar	0.16	0.14
Rb-N_2	0.16	0.14

C. Anomalous contributions to relaxation rates arising from the formation and destruction of bound and quasibound Rb-atom-buffer-gas-atom molecular complexes

Equation (23) predicts the following extrapolated intercepts of $(Z_2 - Z_1)$ at zero buffer-gas pressure:

$$(Z_2 - Z_1)(p=0) = 0.59R_s + 2B_3C_3(B_2 - C_2)^{-1} \quad (I=\tfrac{5}{2}) \tag{26a}$$

$$= 0.50R_s + 2B_3C_3(B_2 - C_2)^{-1} \quad (I=\tfrac{3}{2}). \tag{26b}$$

In our experiment the calculated value of R_s was 7.7 $\sec^{-1}$ (see Ref. 2). The calculated values of the term $2B_3C_3(B_2 - C_2)$ at buffer-gas pressures above 100 Torr were approximately 1.6 $\sec^{-1}$ for Rb^{87} and 0.7 $\sec^{-1}$ for Rb^{85}. We, therefore, would expect that the extrapolated intercepts of the $(Z_2 - Z_1)$ data should occur at approximately 5.4 $\sec^{-1}$ for Rb^{87} and at 5.2 $\sec^{-1}$ for Rb^{85}. In fact, however, the values of these intercepts listed in Table V, and displayed in Figs. 1–3, range from 14.0 to 17.3 $\sec^{-1}$, about three times the anticipated values. We have argued in previous publications that such anomalous contributions to relaxation rates arise from the formation and destruction of bound and quasibound Van der Waals molecular complexes.[2,26] Since D_0, σ, and R_s are now known, we can investigate this possibility further by calculating how much anomalous relaxation R^* must exist at any particular buffer-gas pressure to produce the observed value of Z_2 or Z_3. The results for Rb^{85} and Rb^{87} in He have already been published. The results for Ne are displayed in Fig. 6. The larger uncertainties attached to measurements of Z_2 in Ar and N_2 prevent us from performing a similar reduction of data in these gases.

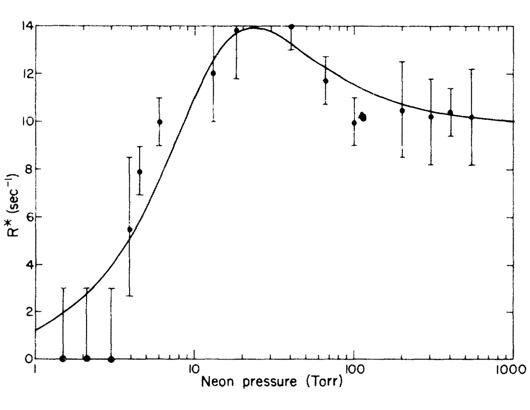

FIG. 6. Evaluated anomalous relaxation R^* in Rb^{85} as a function of Ne pressure, with a fit of Eqs. (9), (10), and (16) to the data. The evaluated parameters are listed in Table VII.

It is not possible to explain R^* on the basis of any conventional relaxation processes. Since R^* becomes constant at high buffer-gas pressures it cannot arise from relaxation in simple alkali-metal-atom–buffer-gas-atom collisions: an effect arising from this source would be proportional to buffer-gas pressure. R^*'s constancy at high buffer-gas pressure, the very small wall relaxation rates at these pressures, and the expectation of minimal contributions from higher-order diffusion modes under conditions of weak pumping, all argue strongly against the possibility of R^* arising from diffusion effects. R^*'s fall to zero at low buffer-gas pressures rules out the possibility that spin exchange might be its cause: an anomalous contribution from spin exchange would remain constant at all buffer-gas pressures. Moreover, in an experiment on Cs it was shown that relaxation rates scaled with the spin-exchange rate about as expected.[26] Since R^* is generally larger than R_s in the experiments performed, other less probable interactions involving two alkali-metal atoms, such as the formation of alkali dimers, can be ruled out as a possible cause of R^*.[28,29] Finally, R^* cannot be attributed to idiosyncrasies of particular experimental techniques: reanalysis of data taken in fully independent experiments confirm the existence of the effect. We discuss examples later in the paper.

We now show that R^* represents relaxation at the hyperfine frequency, ΔW, rather than at the Zeeman frequency, ω_F. From Eqs. (4a) and (4b) we obtain

$$Z_2 - Z_1 \approx \frac{2(2I+1)^2 - 1}{2(2I+1)^2}\left[Cj(\Delta W) + C^*j^*(\Delta W)\right]. \tag{27}$$

For simplicity we have omitted terms involving R_s [see Eqs. (26a) and (26b)]. The term in Eq. (27) involving $Cj(\Delta W)$ is just R, the binary relaxation rate, modified by a nuclear-spin factor. The remaining term, the contribution of anomalous relaxation to $Z_2 - Z_1$, depends only upon $C^*j^*(\Delta W)$. $Z_2 - Z_1$ therefore depends only upon the strength of anomalous relaxation at the hyperfine frequency. Evaluation of the experimental data, based on Eq. (27), rather than on our analyses of Z_2 alone, yields values of R^* within 3% of those displayed in Fig. 6.

Since R^* involves relaxation at the hyperfine frequency, its effects also should be seen in the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$. We confirm this expectation in later sections through reconsideration of previously published data.

Calculations based on Refs. 14 and 15 show that Rb-atom–light-noble-gas-atom Van der Waals molecules form with sufficient frequency to produce the observed anomalous relaxation, provided that the probability for relaxation in such a molecular formation is relatively high, of the order of 10^{-2}. We have already written Eqs. (9) and (10), which should describe the effects of relaxation in quasimolecular collisions. We expect the correlation time τ_c to be related to the rate of collisions of a molecular complex with buffer-gas atoms, and, in some cases, to the natural lifetime of a quasibound state. We thus have

$$1/\tau_c = 1/\tau_0 + n_0\sigma_c v_{\text{rel}}\, p/p_0, \tag{28}$$

where σ_c is an effective cross section associated with the collisional correlation time. Taken together, Eqs. (9), (20), and (28) predict a rather special dependence of R^* upon buffer-gas pressure: zero at low pressure, a rise to a maximum at intermediate pressure, and a retreat to a constant value at high pressure. In Ref. 2 we published computer fits of these equations to the R^* data for Rb^{85}-He and Rb^{87}-He. In Fig. 6 we display the fit for Rb^{85} in Ne. We summarize the evaluated parameters for all three fits in Table VII.

We pointed out earlier that the Rb-He and the Rb-Ne systems differ significantly in the relative numbers of bound and quasibound states. For Rb-Ne and most noble-gas-atom–alkali-metal-atom pairs there are roughly twice as many bound states as quasibound states. For the special case of Rb-He, however, there is one twofold degenerate bound state, and one sixfold degenerate quasibound state. For Rb-He, therefore, relative contributions to R^* from the formation of quasibound molecules should be greater than in Rb-Ne. This expectation is borne out by comparison of the fitted B/C ratios for the two systems. Also, since there is only one quasibound state for Rb-He, we expect to be able to assign a unique lifetime against dissociative tunneling. Our computer analysis yields 6×10^{-10} sec for the Rb^{85} data, and 3×10^{-10} sec for the Rb^{87} data in reasonable agreement with the theoretical value of 3.6×10^{-10} sec calculated by Kiehl.[16] We have explained in Sec. III that the Rb^{87} data is inherently less reliable than that for Rb^{87}. There also are fewer R^* data points for Rb^{87} than for Rb^{85}.[2] We believe that the differences in R^* relaxation parameters evaluated for the two isotopes primarily reflect uncertainties in the Rb^{87} results, rather than a physically interesting effect. In the Rb-Ne case, relatively few of the quasibound states have lifetimes shorter than the inverse of the collisional rate of breakup. We therefore would expect to find no natural lifetime effect in Rb-Ne, within the accuracy of our data. Our computer analysis for Rb-Ne yields this result.

TABLE VII. Parameters evaluated from fits of Eqs. (9) and (10) to R^* data for Rb^{85} and Rb^{87} in He and Ne. See Fig. 3, Ref. 2, and Fig. 7 of this paper.

	B/C (Torr)	$(n_0\sigma_B v_{\text{rel}}/p_0)$ (10^9 sec^{-1} Torr^{-1})	τ (10^{-10} sec)
Rb^{85}-He	95	1.5	5.6
Rb^{87}-He	61	0.51	2.7
Rb^{85}-Ne	20	1.5	...

Finally, we note that if the measured values for $(n_0\sigma_B v_{\text{rel}}/p_0)$ listed in Table VII are converted into cross sections, we obtain values of the order of 10^{-13} cm^2, several times higher than the geometric cross sections ($\approx 10^{-14}$ cm^2). It appears that in these cases the inverse of the correlation time is significantly greater than the quasimolecular breakup rate. We have no present explanation for this effect. (See *Note added in proof.*)

D. Examination of nuclear-spin effects in collisional relaxation: Studies of the "slow" relaxation rate Z_1 of Rb^{85} and Rb^{87} in various buffer gases

The experimental analyses presented so far have been applied to measurements of the "fast" relaxation rate Z_2, or to measurements of the effective single exponential relaxation rate Z_3. Nuclear-spin effects in these cases are rather small: contributions of the various relaxation processes to Z_2 in particular are largely unmodified by nuclear-spin factors. The situation is different in the case of the "slow" relaxation rate Z_1, where nuclear-spin effects play a substantial role. Now that we have independent determinations of all relevant relaxation parameters, we can investigate how well Eqs. (19a), (16a)–(16f), and (17a)–(17f) actually predict the dependence of Z_1 upon buffer-gas pressure.

Before proceeding, we briefly review the anticipated contributions of the various relaxation processes to Z_1. The pumping rate A, and the wall relaxation rate R', are independent of nuclear spin and make the same contribution to Z_1 that they make to Z_2. The contribution of the spin-exchange rate to Z_1 is small: the spin-exchange term $R_s[2(2I+1)]^{-1}$ in C_2 is nearly canceled by the term $B_3C_3(B_2-C_2)^{-1}$. The contribution of the rate for relaxation in simple binary collisions of Rb atoms with buffer-gas atoms R, is modified by the factor $[2(2I+1)]^{-1}$ for normal electron randomization relaxation $[j(\omega_F)=j(\Delta W)]$. This "slowing" factor amounts to $\frac{1}{8}$ for Rb^{87}, and $\frac{1}{18}$ for Rb^{85}. Finally, up to this point we have assumed that the contribution of R^*, the anomalous relaxation rate, to Z_1 also should be describable by equations of the form of Eqs. (4a)–(4c). We want to test the validity of that approximation.

At high buffer-gas pressures the behavior of R^* should become similar to that of R: as the molecular breakup rate increases, the effect of short-lived Rb-buffer-gas molecules upon relaxation should approach the limit provided by simple binary collisions. In addition, the binary relaxation rate itself becomes large compared to the pumping rate, the spin-exchange rate, and the wall relaxation rate. We thus expect that at high buffer-gas pressures the ratios of the relaxation rates, Z_2/Z_1, should approach asymptotic values corresponding to those for electron randomization relaxation, 8:1 for Rb^{87}, and 18:1 for Rb^{85}. In Figs. 7 and 8 we display the measured ratios Z_2/Z_1 for Rb^{85} and Rb^{87} in a variety of buffer gases. The experimental data are compatible with the anticipated asymptotic values. The agreement is demonstrated more dramatically by subtracting the contributions of the pumping, spin-exchange, and wall relaxation rates from the measured Z_2/Z_1 ratios. The results for high pressures of the various buffer gases are summarized below, where we list the modified Z_2/Z_1 ratios and the pressures (in parentheses, in Torr) at which they were measured. The Rb^{85} results cluster about the ratio 18:1, while the Rb^{87} cluster about 8:1, as predicted. The ratio of Rb^{87}-He is anomalously high only because the breakup rate at that pressure is not yet sufficiently high to ensure that the nuclear-spin effects of R^* follow those of sudden binary collisions (we shall touch upon this point again in the discussion to follow):

Rb^{85}-He: 20 (164), 18.5 (270), 19.6 (409), 20 (527);

Rb^{85}-Ne: 16.8 (200), 17.0 (300), 18.2 (400), 18.3 (500);

Rb^{85}-N_2: 18.8 (100), 16.3 (200), 18.4 (250), 17.1 (300);

Rb^{85}-Ar: 17.0 (81), 17.2 (150);

Rb^{87}-He: 13.9 (391);

Rb^{87}-Ne: 9.43 (349), 8.3 (485);

Rb^{87}-N_2: 9.7 (100);

Rb^{87}-Ar: 7.7 (80), 7.2 (150).

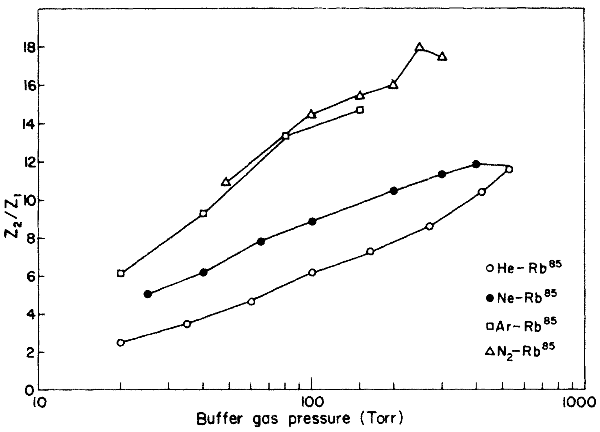

FIG. 7. Measured ratios of rate constants Z_2/Z_1 for Rb^{85} as a function of buffer-gas pressure. The ratios at high pressures approach 18:1 when pumping, wall relaxation, and spin-exchange rates are subtracted out (see text).

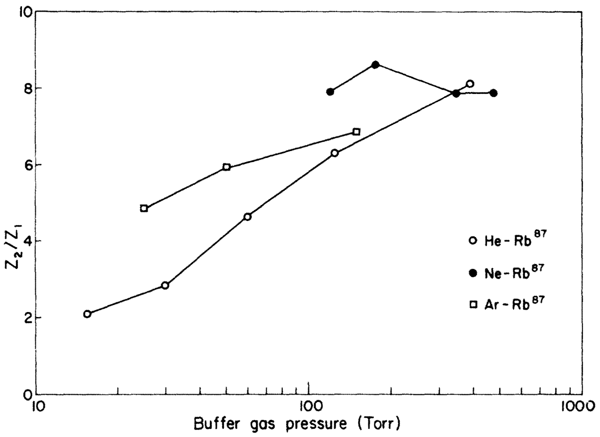

FIG. 8. Measured ratios of rate constants Z_2/Z_1 for Rb^{87} as a function of buffer-gas pressure. The ratios at high pressures approach 8:1 when pumping, wall relaxation, and spin-exchange rates are subtracted out (see text).

We now wish to compare the predicted and measured values of Z_1 throughout the entire range of buffer-gas pressures over which we have measured double exponential pumping transients. In order to do this, we must know the value of the effective pumping rate, $\frac{1}{3}A$, at each particular buffer-gas pressure. Reference to Eqs. (16a)–(16f) and (20a) indicates that $\frac{1}{3}A$ can be determined conveniently through measurement of Z_1 as a function of relative intensity of pumping light. We have made many such measurements, both for Rb^{85} and for Rb^{87}. All of the analyses which follow include appropriate determinations or interpolations of $\frac{1}{3}A$. We thus have fixed all contributions to Z_1, with the exception of that of R^*, the anomalous relaxation rate.

From the curves in Fig. 6 of the present paper and Fig. 3 of Ref. 2 we know the value of R^* at all pressures of He or Ne. Reference to Eqs. (4a) and (4b) and our previous discussion indicate that when $\tau_c \ll \tau_H$, $j(\omega_F) \approx j(\Delta W)$, and R^* should make a contribution of $R^*\,[2(2I+1)]^{-1}$ to C_2. As τ_c becomes longer, $j^*(\omega_F) > j^*(\Delta W)$, and the relative contribution to C_2 should grow. In terms of the present model of nuclear-spin-hyperfine-interaction effects, the ratio of the contribution of R^* to Z_1, relative to its contribution to Z_2, should be bounded by the limits $[2(2I+1)]^{-1}$ and 1.0.

The experimental data provides surprises. In many cases the contribution of R^* to Z_1 is substantially less than the minimum projected in the preceeding paragraph. We provide full particulars in Figs. 9–12, which display the experimental measurements of Z_1 together with theoretical predictions based on the measurements already discussed. For Rb^{85} in high pressures of He and Ne there is excellent agreement between the measured values of Z_1 and those predicted on the assumption that $j^*(\omega_F) = j^*(\Delta W)$ for R^*. At pressures below about 100 Torr, however, the measured values of Z_1 fall *below* the predicted values. If we make the assumption that $j^*(\omega_F) = 0$ for R^* in this pressure range, good agreement is restored. For $Rb^{85}He$ (Fig. 10), the data generally fall between predictions based on $j^*(\omega_F) = j^*(\Delta W)$, and $j^*(\omega_F) = 0$. For Rb^{87} in He and Ne (Figs. 11 and 12), we see that at all pressures studied even the assumption that $j^*(\omega_F) = 0$ is insufficient to secure agreement between theory and experiment. In fact, for the intermediate pressure range, it appears that the assumption that R^* makes a *zero* contribution to Z_1 would be consistent with the data. These results are curious indeed, but are not without precedent: similar behavior for Rb in He has been measured by Aymar, Bouchiat, and Brossel.[30] We, as they, have been unsuccessful at constructing a physically reasonable model which provides the required enhancement of the spectral density function at ΔW, with suppression at ω_F. However, we believe that the present data provides additional keys to the resolution of this question. Figures 9–12 show that the major discrepancies between theory and experiment begin to occur at about 100 Torr. It is just in this pressure range that $2\pi\Delta W\tau_c \approx 1$. We speculate that approximations inherent in the simple nuclear decoupling-recoupling scheme, particularly those related to the treatment of phases, may break down when the correlation time of the collisional perturbation is of the same order of magnitude as the hyperfine period of the free atom.

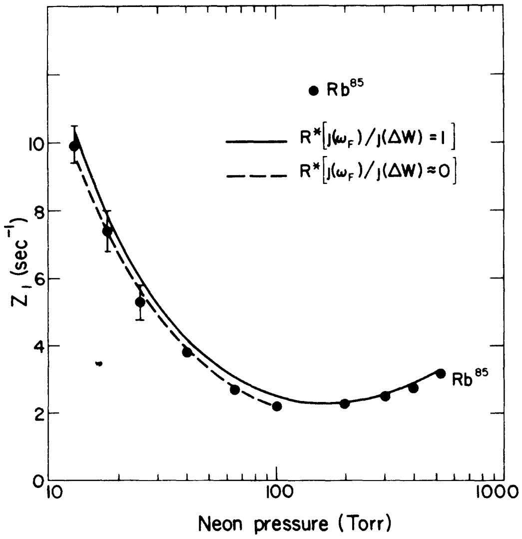

FIG. 9. Measured values of Z_1 for Rb^{85} in Ne. The solid and dashed lines are projections based on values of R, R', R^*, R_S, and A independently determined.

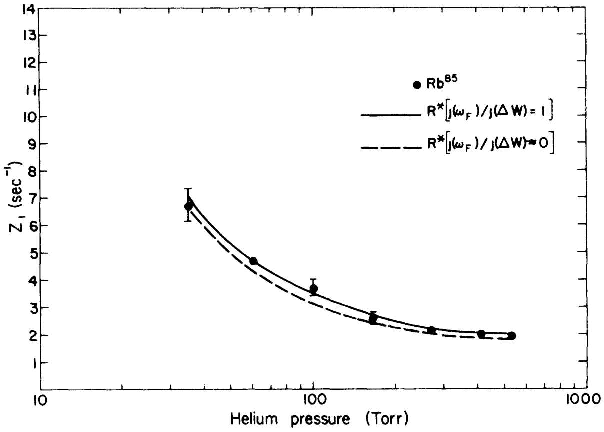

FIG. 10. Measured values of Z_1 for Rb^{85} in He. The solid and dashed lines are projections based on values of R, R', R^*, R_S, and A independently determined.

Aside from the unexpectedly small contribution of R^* to Z_1 at intermediate buffer-gas pressures,

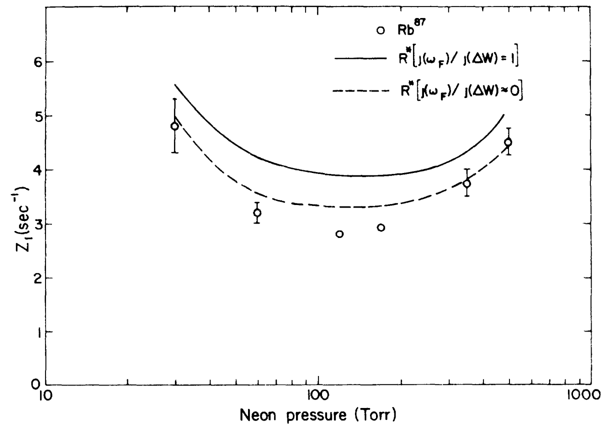

FIG. 11. Measured values of Z_1 for Rb^{87} in Ne. The solid and dashed lines are projections based on values of R, R', R^*, R_S, and A independently determined.

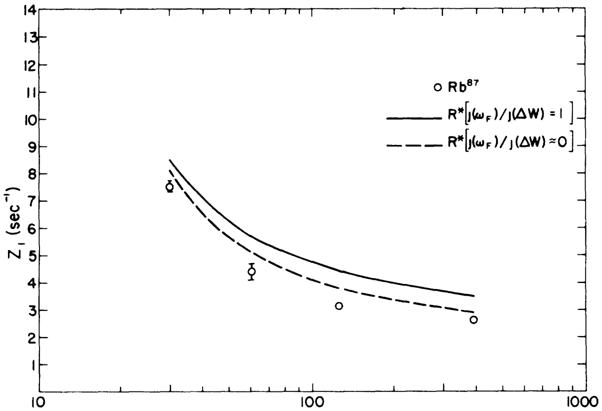

FIG. 12. Measured values of Z_1 for Rb^{87} in He. The solid and dashed lines are projections based on values of R, R', R^*, R_s, and A independently determined.

the anticipated dependence of Z_1 upon buffer-gas pressure is in excellent agreement with the experimental results. Figures 9 and 10, in particular, confirm our determinations of diffusion coefficients and nuclear-spin-independent cross sections for collisional relaxation in Rb-atom–buffer-gas-atom binary collisions.

E. Collisional relaxation within the $5\,^2P_{1/2}$ states of Rb^{85} and Rb^{87}

The rate constants Z_1 and Z_2 of the $\langle S_z \rangle_g$ transient are functions of B_2, B_3, C_2, and C_3 of Eqs. (16a)–(16f) and (17a)–(17f), and therefore depend only upon relaxation processes in the Rb ground state. D_1/D_2, the ratio of the amplitudes of the two exponentials, however, depends also upon B_1 and C_1, the pumping-repopulation rates, and therefore is influenced by relaxation processes within the excited state. In particular, D_1/D_2 depends upon Γ_1, the nuclear-spin-independent rate for the relaxation of $\langle J_z \rangle$ in the $^2P_{1/2}$ excited state. Measurements of D_1/D_2 previously have been utilized in determinations of Γ_1 for relaxation in the $6\,^2P_{1/2}$ state of Cs induced by collisions with He and Ne atoms.[26]

The existence of different nuclear spins in Rb^{85} and Rb^{87} provides opportunities for checks of the D_1/D_2 method of measurement of excited state relaxation and for additional cross checks of the validity of the treatment of nuclear-spin effects in collisional relaxation. In particular, inspection of Tables I–IV shows that under otherwise similar conditions the D_1/D_2 ratios for the two isotopes can differ markedly. According to theory, these differences should be wholly attributable to nuclear-spin effects. We now wish to determine whether unique cross sections σ_1(Rb-He) and σ_1(Rb-Ne) can be found which yield the observed dependence of D_1/D_2 on buffer-gas pressure for *both* Rb isotopes.

TABLE VIII. Values of $\Gamma_1\tau$ (relaxation rate times natural lifetime) and σ_1 (nuclear-spin-independent cross section for the relaxation of $\langle J_z \rangle$ in the Rb $5\,^2P_{1/2}$ state) as determined from analyses of the D_1/D_2 ratio for the $\langle S_z \rangle_g$ optical-pumping transients of Rb^{85} in He.

	p(He) (Torr)	$\Gamma_1\tau$	σ_1 (10^{-16} cm^2)
Rb^{85}-He	164	7.0	3.4
Rb^{85}-He	270	11.0	3.3
Rb^{85}-He	409	18	3.5

While Eq. (22), which describes D_1/D_2, is a cumbersome function of all relaxation parameters, in fact all of these parameters, save $\Gamma_1\tau$, now are fixed by the measurements and analyses we already have discussed. We therefore are concerned with a one-parameter fit. In order to minimize the cumulative uncertainty in analyzing D_1/D_2, we use directly measured quantities wherever possible. For example, since the term $B_3C_3(B_2 - C_2)^{-1}$ turns out to be essentially constant for all (high) buffer-gas pressures (≈ 0.33 for Rb^{85} and ≈ 0.80 for Rb^{87}), we can use Eqs. (20a) and (20b) to evaluate B_2 and C_2 directly from Z_2 and Z_1. We thus avoid the necessity of knowing the exact value of the pumping rate. Moreover, since either the term B_1 or C_1 appears once in every term of the numerator and denominator of Eq. (22), all other dependence of D_1/D_2 on the magnitude of the pumping rate cancels out. The value of C_3 is fixed entirely by the spin-exchange rate. The only remaining difficulty is that because the nuclear-spin effects associated with R^* are not yet fully understood, we may not know the correct contribution of R^* to B_3. Such ambiguities should disappear at buffer-gas pressures high enough to ensure rapid breakup of molecular complexes. We therefore hope for consistent determinations of Γ_1 at high pressures of He and Ne, but do not expect meaningful results at intermediate pressures where Z_1 is imprecisely predicted.

TABLE IX. Values of $\Gamma_1\tau$ (relaxation rate times natural lifetime) and σ_1 (nuclear-spin-independent cross section for the relaxation of $\langle J_z \rangle$ in the Rb $5\,^2P_{1/2}$ state) as determined from analyses of the D_1/D_2 ratio for the $\langle S_z \rangle_g$ optical-pumping transients of Rb^{85} and Rb^{87} in Ne.

	p(Ne) (Torr)	$\Gamma_1\tau$	σ (10^{-16} cm^2)
Rb^{85}-Ne	200	5	4.2
Rb^{85}-Ne	300	10	5.6
Rb^{85}-Ne	400	16	6.7
Rb^{85}-Ne	535	22	6.9
Rb^{87}-Ne	349	10	4.8
Rb^{87}-Ne	485	15	5.2

In Table VIII we summarize the values of $\Gamma_1\tau$ determined from measurements of D_1/D_2 for Rb^{85} in He, which yield an average value of 3.4×10^{-16} cm^2 for σ_1(Rb-He) in the $5\,^2P_{1/2}$ state of Rb. Reference to Fig. 12 and the discussion above suggests that our analysis is not well suited to the Rb^{87}-He data: even at 391 Torr, and even with the assumption that $j(\omega_F)=0$, the value of Z_1 is not predicted as accurately as desired.

In Table IX we summarize the values of $\Gamma_1\tau$ determined from measurements of D_1/D_2 for Rb^{85} in Ne at pressures of 200 Torr and more. Figure 9 suggests that nuclear-spin effects in this case are described quite well by Eqs. (4a) and (4b), with $j^*(\omega_F)=j^*(\Delta W)$ for R^*. This system therefore should be a good candidate for D_1/D_2 analyses. In fact, we find excellent consistency throughout determinations for Ne pressures, with an average value of 5.9×10^{-16} cm^2 for σ_1(Rb-Ne). In the case of Rb^{87} in Ne, Fig. 11 shows that best agreement between theoretical and experimental values of Z_1 are obtained under the assumption that $j(\omega_F)=0$. The average of the values of σ_1 evaluated on this basis listed in Table VIII is 5.0×10^{-16} cm^2, in reasonable agreement with the determinations from the Rb^{85} data.

The values for σ_1 reported above are several times smaller than those found in level crossing experiments by Gallagher[31] and by Bulos and Happer.[32] The discrepancy merits further investigation. There is a difficulty with our experiment which should be borne in mind, however. Although by making measurements at high buffer-gas pressures we minimize uncertainties due to R^* effects, we also work in a region where the D_1/D_2 ratio is a rather insensitive function of $\Gamma_1\tau$. Our confidence in the final values of σ_1 which we report comes mainly from the reproducibility of results obtained over a relatively wide range of buffer-gas pressures, and from the agreement between the values for Rb^{85} and Rb^{87}. On the other hand, we are aware of no nuclear-spin-dependent–population-monitoring experiment, other than the present one, which provides a cross comparison with the Gallagher–Bulos-Happer results. Measurement of the collisional depolarization of resonance radiation at low magnetic fields would be of considerable interest in this regard. The appropriate nuclear spin corrections for such an experiment have been provided in Ref. 25.

V. COMPARISONS WITH OTHER EXPERIMENTS

A. Measurements of the relaxation of $\langle S_z\rangle$ in the presence of rapid spin exchange

In 1965, Franz measured relaxation rates of natural Rb (72% Rb^{85}, 28% Rb^{87}) in the noble gases at a temperature of 67 °C, corresponding to a spin-exchange rate of approximately 168 sec^{-1}.[33] Equation (19b) shows that Z_2 therefore was always greater than 100 sec^{-1}, corresponding to a relaxation time of less than 10 msec. Since this time was shorter than the shutter risetime, and since the fastest relaxation time measured was longer than 50 msec, it is clear that a superposition of the Z_1's for the two isotopes actually was measured. We have calculated the Z_1's expected for Rb^{85} and Rb^{87} in He and Ne in that experiment on the basis of our present results. We have assumed that σ remains constant from 32 to 67 °C, and that the diffusion coefficients are proportional to $T^{3/2}$. We also have assumed that at any particular buffer-gas pressure R^* makes approximately the same contributions to Z_2 and Z_1 as indicated experimentally in the present work. Finally, having found that the Z_1's thus calculated for Rb^{85} and Rb^{87} at any particular buffer-gas pressure turn out to differ by a factor of 1.5 or less, we have approximated the relaxation rate for natural Rb as the weighted average of the Z_1's for the two isotopes. The results of these calculations, along with the relevant 1965 data at high and low pressures of He and Ne, are listed in Table X. The agreement for Ne is well within the bounds of this rather rough calculation: the 1965 measurements are predicted to within 10%. The agreement for He is less impressive, probably because the very small relaxation rates predicted in this buffer gas are influenced to a relatively greater degree by errors in extrapolation from quite different experimental conditions. The cross sections quoted in Franz's paper, 3.3×10^{-25} cm^2 for Rb-He, and 3.3×10^{-24} cm^2 for Rb-Ne, were obtained from data analyses in which the then customary, but incorrect, assumption of "uniform relaxation" was applied to alkali-atom–buffer-gas-atom collisions. The correct values, which as we have shown accurately describe the 1965 results, are the nuclear spin independent cross sections reported in the present paper.

Additional comparisons with previous measure-

TABLE X. Comparison of representative relaxation rates measured for natural Rb at 67 °C (Ref. 33) with calculations of these rates based on the relaxation parameters determined in the present paper.

	P (Torr)	Z meas. (sec^{-1})	Z calc. (sec^{-1})	% difference
Rb-Ne	29.4	6.85 ± 0.23	6.42	7%
Rb-Ne	250	2.44 ± 0.10	2.53	4%
Rb-He	88	3.60 ± 0.21	4.12	14%
Rb-He	236	1.69 ± 0.14	2.15	27%

ments of $\langle S_z \rangle_g$ relaxation can be made. In 1962, Bernheim measured rates for the relaxation of natural Rb in He at a temperature of 50 °C, with techniques and analyses similar to those described in the preceding paragraphs.[34] Since uniform relaxation was assumed, Bernheim's reported cross section, $\sigma(\text{Rb-He}) = 6.2 \times 10^{-25}$ cm^2, is unreliable. Bernheim's data, however, are reproduced quite well when calculated on the basis of the present relaxation parameters. At 87 Torr, Bernheim measured approximately 3.1 sec^{-1} for Z_1: we calculate 3.1 sec^{-1}. At 300 Torr, Bernheim measured approximately 1.5 sec^{-1} for Z_1: we calculate 1.4 sec^{-1}.

We also have reexamined the Rb-Ne and Rb-Ar data from Franzen's 1959 experiment.[22] We find that the relaxation transients under the conditions of that experiment should have contained a mixture of significantly different Z_1's and Z_2's for both isotopes. Since the reported data were obtained from single exponential fits, which in this case should have yielded rather severely distorted results, we are unable to provide meaningful comparisons with the present work.

B. Previous measurement of the relaxation of $\langle S_z \rangle_g$ in He

In 1969, Aymar, Bouchiat, and Brossel (ABB) measured relaxation rates of Rb^{85} and Rb^{87} in He^4 and He^3 buffer gases, at pressures from 16 to 700 Torr.[30] Their experimental technique was very similar to ours: it differed mainly in the fact that strong rather than weak pumping was employed. ABB reported a value of 0.42 for $D_0(\text{Rb-He}^4)$ at 300 °K, the same value found by us. They reported a value of 8.2×10^{-24} cm^2 for $\sigma_e(=\sigma)$, which corresponds to our own value of 3.1×10^{-24}. They also reported ratios $\sigma_e/\sigma_n(\text{Rb}^{87}\text{-He}) \simeq 18$, and $\sigma_e/\sigma_n(\text{Rb}^{85}\text{-He}) \simeq 30$. The σ_e/σ_n ratios are equivalent to the Z_2/Z_1 ratios in our experiment, calculated with R_s, R', and $\frac{1}{3}A$ contributions removed. As we have seen, we obtain $Z_2/Z_1(\text{Rb}^{87}\text{-He}) \approx 8$, and $Z_2/Z_1(\text{Rb}^{85}\text{-He}) \approx 18$. We now shall show that the apparent disagreements between ABB's results and ours disappear when ABB's data is reconsidered in the light of present knowledge.

The main difficulty with ABB's analysis is that they considered neither the effects of spin exchange, nor the anomalous relaxation rate R^* on the fast relaxation rate in $\langle S_z \rangle$ relaxation. The data in ABB's Fig. 6, therefore, contains contributions from relaxation mechanisms other than just wall relaxation and simple buffer-gas relaxation, but was not analyzed for them. In order to make up for these contributions, the evaluated σ_e turned out to be spuriously high. One can get a rough idea of the "true" cross section by estimating the slope of the relaxation rate at He pressures above 200 Torr: one finds a value of σ_e roughly half of that quoted by ABB. Even this value is probably somewhat high, however, due to the fact that ABB's measurements were made over a fairly broad range of vapor pressures, and therefore over a range of spin-exchange rates. Since the highest vapor pressures were employed at the highest buffer-gas pressures, spin-exchange contributions would not be constant, but would make a positive contribution to the slope, and thus artificially inflate the evaluated σ_e. It seems clear that the "true" value of σ_e in ABB's experiment is not the 8.2×10^{-24} cm^2 quoted, but rather is reasonably close to our value of 3.1×10^{-24} cm^2.

We have noted in an earlier section that while the fast relaxation rate is affected by spin exchange, the slow relaxation rate is not. Furthermore, we have seen in Fig. 12 that for Rb^{87}-He in particular, R^* makes a far smaller contribution than anticipated to the "long" relaxation rate Z_1. We expect, then, that ABB's measurements of the long relaxation rate of Rb^{87} in He should be relatively unaffected by R^* and R_s, and therefore should be determined almost entirely by wall relaxation and electron randomization relaxation in Rb-He binary collisions, the latter being modified by the expected nuclear-spin factor $[\frac{1}{2}(2I+1)^2]^{-1}$. We therefore would expect that for $\sigma_n(\text{Rb}^{87}\text{-He})$ ABB should obtain our value of σ, divided by 8, or 0.39×10^{-24} cm^2. In fact ABB found 0.47×10^{-24} cm^2. More-careful calculations show that this small difference is caused by residual contributions to ABB's result from R^*. ABB's long-relaxation-rate data for Rb^{85}-He is similarly explained by the results presented here.

In summary, when spin exchange and R^* effects are taken into account, ABB's data is compatible with the nuclear-spin-independent cross section for $\langle S_z \rangle$ relaxation in binary collisions determined in the present experiment, $\sigma(\text{Rb-He}) = 3.1 \times 10^{-24}$ cm^2. Their *total* measured relaxation rates are strongly affected by R^*, as are ours. When only contributions from binary Rb-atom–buffer-gas-atom collisions are considered, ABB's data is consistent with the theoretical ratios 8:1 for $\sigma_e/\sigma_n(\text{Rb}^{87}\text{-He})$ and 18:1 for $\sigma_e/\sigma_n(\text{Rb}^{85}\text{-He})$, rather than the values 18:1 and 30:1 originally quoted.

C. Measurements of the longitudinal and transverse relaxation of $\langle \vec{S}\cdot\vec{I} \rangle$ of Rb^{85} and Rb^{87} in various buffer gases

In 1974, Vanier, Simard, and Boulanger (VSB) used a Rb maser to measure the relaxation of Rb^{85} in He, Ne, Ar, and N$_2$ buffer gases, at pressures up to about 70 Torr.[35] In order to determine the diffusion coefficients and relaxation cross sections,

TABLE XI. Rough estimations of possible anomalous relaxation effects in $\langle\vec{S}\cdot\vec{I}\rangle$ relaxation data. "Const." represents the constant additive term necessary to reproduce the fitted curves of Vanier *et al.* (Ref. 35) R_s is our estimate of the maximum value of the spin-exchange rate in their experiment. The difference, $R^*(\vec{S}\cdot\vec{I})$ is compared with $R^*(S_z)$, as determined in the present experiment. All units are sec^{-1}.

	Const.	R_s	$R^*(\vec{S}\cdot\vec{I})$	$R^*(S_z)$
He	15.6	4.5	11.1	9.5
Ne	9.8	4.5	5.3	11.5
Ar	16	4.5	11.5	12.5
N_2	12.1	4.5	7.6	12.8

VSB fit the following equation to their data:

$$Z(\vec{S}\cdot\vec{I}) = \left(\frac{\pi^2}{r^2}\right) D_0 \frac{p_0}{p} + n_0\sigma\langle\vec{S}\cdot\vec{I}\rangle\, \bar{V}_{\rm rel}\, \frac{p}{p_0} + R_s\,. \qquad (29)$$

By allowing the spin-exchange rate R_s to be a variable parameter, VSB's analysis would have obscured the presence of anomalous relaxation. We give a rough idea of this possibility in Table XI, where we estimate the value of the constant additive term necessary to reproduce VSB's fits, and compare it to our own estimate of the actual spin-exchange rate in their experiment. The results of a more careful analysis for Rb^{85}-He have been published in Ref. 2, where it has been shown that the anomalous relaxation rates extracted from VSB's data follow quite well the R^* values extracted from the $\langle S_z\rangle$ data.

Due to the relatively small contributions to relaxation rates from Rb-He and Rb-Ne binary collisions at low He or Ne pressures, VSB were able to determine relaxation cross sections only for Rb colliding with Ar and N_2. We compare their results with ours in Table XII. Since VSB's technique of curve fitting effectively places most of the high-pressure contributions of R^* into the fitted R_s, and since the rates for relaxation in binary Rb-Ar or Rb-N_2 collisions are large relative to contributions from other sources, VSB's determinations of $\sigma\langle\vec{S}\cdot\vec{I}\rangle$ for Ar and N_2 should be reasonably accurate. We have estimated that if only the slope of their higher-pressure Ar data were used to evaluate $\sigma\langle\vec{S}\cdot\vec{I}\rangle$, the new value would be only about 10% higher, nevertheless significantly closer to our own determination of $\sigma\langle S_z\rangle$. We recall that for sudden binary collisions $[j(\omega_F)=j(\Delta W)]$, theory predicts that $\sigma\langle\vec{S}\cdot\vec{I}\rangle$ should be equal to $\sigma\langle S_z\rangle$. The results in Table X confirm this expectation.

TABLE XII. Comparison of cross section for the relaxation of $\langle\vec{S}\cdot\vec{I}\rangle_g$ (Ref. 35) with the cross sections for the relaxation of $\langle S_z\rangle_g$ reported in the present paper. Theory predicts the two cross sections should be equal.

	$\sigma\langle\vec{S}\cdot\vec{I}\rangle$ (10^{-24} cm^2)	$\sigma\langle S_z\rangle$ (10^{-24} cm^2)
Rb-Ar	490	630
Rb-N_2	80	83

TABLE XIII. Comparison of diffusion coefficients determined by measurement of (a) relaxation of $\langle\vec{S}\cdot\vec{I}\rangle$ (Ref. 35); (b) relaxation of coherence of $\langle\vec{S}\cdot\vec{I}\rangle$ (Ref. 35); (c) relaxation of $\langle S_z\rangle_g$ (Ref. 2); (d) present work. All units are cm^2/sec.

	D_0 (27 °C)	D_0 (32 °C)
Rb-He	0.32^a	0.42^d
	0.42^b	0.42^c
Rb-Ne	0.16^a	0.23^d
	0.20^b	
Rb-Ar	0.14^a	0.16^d
	0.15^b	
Rb-N_2	0.13^a	0.16^d
	0.15^b	

VSB also determined diffusion coefficients for Rb in the various buffer gases. In our analysis of $\langle S_z\rangle_g$ data, we found that the anomalous relaxation rate decreases at low buffer-gas pressures. In VSB's analysis, however, a constant (anomalous) rate is subtracted off at all buffer-gas pressures. As a result, VSB attribute somewhat less of measured relaxation rates at low buffer-gas pressures to wall relaxation than we do. The effective diffusion coefficients evaluated by VSB therefore may be expected to be slightly smaller than ours. We compare the results of the two experiments in Table XIII.

In 1964, Arditi and Carver measured relaxation rates of $\langle\vec{S}\cdot\vec{I}\rangle$, of Rb^{87} in 14 Torr of He, in 10 and 50 Torr of Ne, and in 5 and 30 Torr of Ar, from which they deduced values of D_0 for Rb in He, Ne, and Ar, and values of $\sigma\langle\vec{S}\cdot\vec{I}\rangle$ for Rb in Ne and Ar.[36] These diffusion coefficients and cross sections should be equal to those found in the present ex-

TABLE XIV. Rates of relaxation of $\langle\vec{S}\cdot\vec{I}\rangle$ as measured in Ref. 36, compared to values calculated on the basis of results reported in the present paper.

Buffer gas	$(1/T_1)$ meas. (sec^{-1})	$(1/T_1)$ calc. (sec^{-1})
14-Torr He	32	37
10-Torr Ne	23	23
50-Torr Ne	23	19
30-Torr Ar	42	45

periment. In fact, however, the apparent discrepancies are large. For example, whereas we have measured 19×10^{-24} cm^2 for σ(Rb-Ne), Arditi and Carver's analysis yields a value of 1600×10^{-24} cm^2! This spectacular disagreement disappears when R^* effects are taken into account. We have calculated the values of $(1/T_1)$ that would be expected in Arditi and Carver's experiment on the basis of the results in the present paper. Since their results were extrapolated to zero rate of spin exchange, we have

$$1/T_1 = R + R' + R^* , \tag{30}$$

where R, R', and R^* are defined in Eqs. (7), (14), and (9), respectively. In Table XIV we display the striking agreement between the newly calculated values and the experimental results.

VI. SUMMARY

The results of this experiment clarify our understanding of electronic and nuclear-spin relaxation within the ground state of an alkali-metal atom. By measuring optical-pumping transients at very high buffer-gas pressures, we have determined accurate cross sections for $\langle S_z\rangle$ relaxation in simple binary Rb-atom–buffer-gas-atom collisions. By measuring transients in the limit of very-low buffer-gas pressures, we have found the diffusion coefficients for Rb in the various buffer gases. Utilizing these results, we have analyzed measurements at intermediate buffer-gas pressures, extracting those contributions to relaxation rates arising from the formation of Van der Waals molecular complexes. At He and Ne pressures of less than 100 Torr, the quasimolecular relaxation rate has been shown to be as much as an order of magnitude greater than the normal binary relaxation rate. This discovery has led to the resolution of many apparent puzzles and anomalies in earlier experiments. When binary relaxation, quasimolecular relaxation, wall relaxation, and spin exchange are properly taken into account, the electronic spin relaxation of Rb has been shown to be described well over a wide range of circumstances.

Note added in proof. We noted in Sec. IV C that the cross sections evaluated for τ_c in R^* relaxation are significantly larger than the geometric values. The corresponding factors B and C in Eq. 10 for Rb^{85}-He, for example, are $B = 1.8\times10^{20}$ Hz Torr^{-1}, and $C = 1.9\times10^{18}$ Hz^3 Torr^{-2}. Since B and C can be represented by $(2/3)(\Delta\omega)^2(T_F)^{-1}$,[5] one can calculate from either parameter the strength of the collisional perturbation $\Delta\omega$ if the appropriate formation rate $(T_F)^{-1}$ is known. From Baylis' Rb–He potential parameters, we have $\epsilon_0 = 1.84\times10^{-16}$ erg, and $R_m = 7.36\times10^{-8}$ cm.[15] Using Mahan's formulation,[14] we calculate $(T_F)^{-1}$, the rate of complex formation in three-body collisions, to be $0.70p^2$, assuming the breakup cross section to be 1×10^{-14} cm^2. Noting that $R^* \approx 8$ sec^{-1} at high p, we obtain $\Delta\omega \sim 2\times10^9$ Hz. We have used the same potential parameters, along with the calculations of Kiehl,[16] to estimate the rate of formation of complexes in two-body collisions, $(T_F')^{-1}$. We obtain $(T_F')^{-1} \approx 40p$, which, taken with the value of B above, yields $\langle\Delta\omega\rangle \approx 2.6\times10^9$ Hz. While the two values of $\langle\Delta\omega\rangle$ thus determined are consistent, they also are rather large. The high-pressure measurements alone yield results that appear more reasonable. Considering the high-pressure limit of R^* in Rb–He to be 8 sec^{-1}, for example, and taking $\sigma_c = \sigma_B = 1\times10^{-14}$ cm^2, we obtain $\langle\Delta\omega\rangle \sim 174$ MHz, based on the $(T_F)^{-1}$ given above. We conclude that more sophisticated analyses of R^* data may provide substantially different values of B, C, and σ_c. We hope that the initial results may stimulate a more definitive theoretical attack on this problem.

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[1] For a review of many theoretical and experimental aspects of optical pumping, see W. Happer, Rev. Mod. Phys. 44, 169 (1972).

[2] F. A. Franz and C. Volk, Phys. Rev. Lett. 35, 1704 (1975).

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

[4] C. C. Bouchiat and M. A. Bouchiat, Phys. Rev. A 2, 1274 (1970).

[5] M. A. Bouchiat, J. Brossel, and L. C. Pottier, J. Chem. Phys. 56, 3703 (1972).

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

[7] H. G. Dehmelt, Phys. Rev. 105, 1487 (1957).

[8] P. L. Bender, thesis (Princeton University, 1956) (unpublished).

[9] M. A. Bouchiat, J. Phys. (Paris) 24, 370 (1963); 24, 611 (1963).

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

[11] F. Masnou-Seeuws and M. A. Bouchiat, J. Phys. 28,

406 (1967).

[12] F. A. Franz and C. E. Sooriamoorthi, Phys. Rev. A 8, 2390 (1973).

[13] C. P. Slichter, *Principles of Magnetic Resonance*, (Harper & Row, New York, 1963), p. 141, Eq. (37).

[14] G. Mahan, J. Chem. Phys. 52, 258 (1970).

[15] W. E. Baylis, J. Chem. Phys. 51, 2665 (1969); corrected values by private communication.

[16] J. T. Kiehl, Phys. Lett. 56A, 82 (1976), and private communication.

[17] W. E. Baylis, Phys. Rev. A 1, 990 (1970).

[18] F. Grossetete, J. Phys. (Paris) 25, 383 (1964); 29, 456 (1968).

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

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

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

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

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

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

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

[26] F. A. Franz and C. E. Sooriamoorthi, Phys. Rev. A 10, 126 (1974).

[27] L. W. Anderson, Nuovo Cimento 31, 986 (1964).

[28] H. G. Weber, H.-J. Glas, R. Huber, M. Kompitsas, G. Schmidt, and G. Zu Putlitz, Z. Phys. 268, 91 (1974).

[29] R. Gupta, W. Happer, G. Moe, and W. Park, Phys. Rev. Lett. (to be published).

[30] M. Aymar, M. A. Bouchiat, and J. Brossel, J. Phys. (Paris) 30, 619 (1969).

[31] A. Gallagher, Phys. Rev. 157, 68 (1967).

[32] R. B. Bulos and W. Happer, Phys. Rev. A 4, 849 (1971).

[33] F. A. Franz, Phys. Rev. 139, A603 (1965).

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

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

[36] M. Arditi and T. R. Carver, Phys. Rev. 136, A643 (1964).