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Alkali-Rare-Gas van der Waals Molecules and Ground-State Relaxation Processes in Optical Pumping

C. C. Bouchiat*
Laboratorie de Physique Thêorique et Hautes Energies, Facultê des Sciences,
Orsay, France

and

M. A. Bouchiat
Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supêrieure,
*Facultê des Sciences, Paris, France**

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Relaxation experiments performed on alkali atoms polarized in their ground state by optical pumping in the presence of a rare gas have been previously reported and interpreted. It was shown that the relaxation governed by the spin-orbit interaction is strongly affected by the formation of chemically unstable Rb-Kr molecules bound by van der Waals forces. The previous theoretical analysis, restricted to the longitudinal relaxation, is extended here to relaxation processes involving the transverse components of the electronic polarization and hyperfine "coherences" (elements of the density matrix between different hyperfine states). The effects resulting from the action of a rf field are also examined. The main results of this work, among others, are (a) the prediction of a Zeeman transition-line pressure shift, in some circumstances larger by several orders of magnitude than the one calculated by Herman, and having a very peculiar variation with the rare-gas pressure; (b) a quantitative explanation of the anomalous pressure dependence of the hyperfine transition linewidth discovered by Bender and Cohen; (c) a proposal of a method of detection of rf transitions between states of the alkali–rare-gas molecules by their effect on the relaxation process.

INTRODUCTION

It has been shown recently[1,2] that the relaxation of the longitudinal polarization of ground-state alkali atoms in a rare-gas medium is strongly affected by the presence of alkali–rare-gas molecules bound by van der Waals forces. An alkali atom has a certain probability to be captured by a rare-gas atom into a molecular state during a three-body collision. During the lifetime of the molecule likely to be destroyed at the next collision, the electronic spin $\vec{S}$ is subjected to the molecular spin-orbit interaction $\gamma\vec{S}\cdot\vec{N}$ ($\vec{N}$ is the relative orbital momentum of the two bound atoms). This type of collision, called "sticking" collision in Ref. 1, is a very efficient relaxation mechanism, especially when the polarization $\langle\vec{S}\rangle$ has enough time to perform a complete precession around $\vec{N}$. Up to now, the experimental and theoretical analysis of the "sticking" collisions has been restricted to the relaxation of the component of $\langle\vec{S}\rangle$ along the dc field (longitudinal relaxation). Apart from being, of course, unambiguous evidence for the very existence of alkali–rare-gas molecules, this analysis has led already to a number of interesting results: a determination of the chemical equilibrium constant for the reaction $\mathrm{Rb}+\mathrm{Kr}\rightleftharpoons\mathrm{Rb}-\mathrm{Kr}$, the strength of the spin-orbit coupling, etc. The purpose of the present work is to extend it to effects involving the transverse components of $\langle\vec{S}\rangle$ or resulting from the action of a rf field.

In Sec. I, we derive the master equation for the density matrix of an ensemble of paramagnetic atoms subjected to the "sticking" collision mechanism. In particular, we shall obtain the transverse relaxation time T_2, and the Zeeman transition-line shift $\delta\omega$. Their very peculiar dependence upon the dc field, and the rare-gas pressure is discussed in detail. The most remarkable features are the comparatively large value of the shift $\delta\omega$, and the occurrence at a given pressure of a change of its sign. A comparison is given with the shifts produced by other effects involving the alkali–rare-gas interaction.[3] Finally, we show briefly that the mechanism discussed in this paper is practically irrelevant to the muonium experiments.[4]

In Sec. II, we turn our attention to the evolution of hyperfine "coherences" (elements of the density matrix between different hyperfine states). The role of the spin-orbit interaction, and of the isotropic hyperfine interaction are examined separately. The anomalous pressure dependence of the hyperfine transition linewidth found experimentally by Bender and Cohen[5] is explained quantitatively in the light of our results.

Section III is devoted to the analysis of the combined actions of a rf field, and of "sticking" collisions on an ensemble of alkali atoms. From our discussion, there emerge two different cases: (a) The frequency of the rf field is very close to the Zeeman frequency of the free atom, and very far from the resonance frequencies of the bound atoms. The Bloch equations are shown to hold with the relaxation parameters obtained in Sec. I. (b) The rf-field frequency falls among the resonance frequencies of the bound atom, but far from that of the free atom. The relaxation process is found to be significantly affected by the action of the rf field on the bound alkali atoms, allowing a detection of rf transitions between states of the alkali–rare-gas molecules.

I. TRANSVERSE RELAXATION AND LINE SHIFT INDUCED BY COLLISIONS LEADING TO BOUND AND METASTABLE STATES

In this section, we shall extend to the transverse components $\langle S_\pm\rangle=\langle S_x\pm iS_y\rangle$ of the electronic polarization the analysis performed for the longitudinal one $\langle S_z\rangle$ in Ref. 1 where a complete description of the relaxation model was given (Ref. 1, Sec. V). We shall follow closely the notations of this paper. As in Ref. 1, we divide the ensemble of alkali atoms under study into two classes.

(a) The fraction $\Delta t/T_f$ of atoms which get bound to rare-gas atoms at an instant t_0 falling in the time interval $(t, t+\Delta t)$. Δt is assumed to be much smaller than the inverse of the molecular formation rate T_f and much larger than the mean lifetime τ of the molecular state (typical orders of magnitude are $\tau\approx 5\;10^{-8}$ sec/Torr^{-1}, $T_f\approx 10^{-2}$ sec/Torr^{-2}).

(b) The fraction $1-\Delta t/T_f$ of those which remain free during the same time interval.

Let $\psi(t)$ be the wave function of an atom of class (a). Between t and t_0 (the instant of the molecule formation), the evolution of $\psi(t)$ is governed by the free Hamiltonian $\mathcal{H}_0=\gamma_S\,\vec{S}\cdot\vec{H}_0$; between t_0 and t_0+T (the instant at which occurs the molecular breaking) it is governed by $\mathcal{H}=\gamma_S\,\vec{S}\cdot(\vec{H}_0+\vec{H}_1)$, where $\vec{H}_1$ is the effective magnetic field representing the molecular spin-orbit coupling; and between t_0+T and $t+\Delta t$ it is governed by $\mathcal{H}_0$ again. It will be convenient to use the interaction representation $\tilde{\psi}(t)=e^{i\hbar^{-1}\mathcal{H}_0 t}\psi(t)$. The wave function $\tilde{\psi}(t+\Delta t)$ is given in terms of $\tilde{\psi}(t)$ by

$$\tilde{\psi}(t+\Delta t)=\tilde{\mathfrak{U}}(t_0, T, \vec{H}_1)\,\tilde{\psi}(t)\quad, \tag{1.1}$$

with

$$\tilde{\mathfrak{U}}(t_0, T, \vec{H}_1)=e^{i\hbar^{-1}\mathcal{H}_0 t_0}e^{i\hbar^{-1}\mathcal{H}_0 T}\times e^{-i\hbar^{-1}\mathcal{H}T}e^{-i\hbar^{-1}\mathcal{H}_0 t_0}\quad. \tag{1.2}$$

In the interaction representation the density matrix of class (b) atoms is stationary while that of atoms of class (a) is subjected to an evolution governed by $\tilde{\mathfrak{U}}(t_0, T, \vec{H}_1)$. The density matrix of the whole ensemble of atoms at time $t+\Delta t$ is then given as follows:

$$\tilde{\rho}(t+\Delta t)=(1-\Delta t/T_f)\,\tilde{\rho}(t)+\Delta t/T_f\times\langle\tilde{\mathfrak{U}}(t_0, T, \vec{H}_1)\,\tilde{\rho}(t)\,\tilde{\mathfrak{U}}^\dagger(t_0, T, \vec{H}_1)\rangle_{\mathrm{av}}\quad. \tag{1.3}$$

The average is to be performed over the stochastic variables t_0, T, and $\vec{H}_1$. Since all configurations of the magnetic field $\vec{H}=\vec{H}_0+\vec{H}_1$ obtained by any rotation R around $\vec{H}_0$ are equiprobable, we can without affecting the final result replace $\tilde{\mathfrak{U}}$ by $U(R)\times\tilde{\mathfrak{U}}\,U^{-1}(R)$, where $U(R)$ is the unitary operator associated with R. Taking $U(R)=e^{-i\hbar^{-1}\mathcal{H}_0 t_0}$, we remove the dependence upon t_0 which after taking the average would have given a dependence upon Δt.

With the time interval Δt occurring only in the form of the factor $\Delta t/T_f \ll 1$, we can write a differential equation for $\tilde{\rho}$:

$$\frac{\partial\tilde{\rho}}{\partial t} = -\frac{1}{T_f}\,[\tilde{\rho}(t) - \langle\, V(T,\vec{\mathrm{H}}_1)\,\tilde{\rho}(t)\,V^{\dagger}(T,\vec{\mathrm{H}}_1)\,\rangle_{\mathrm{av}}\,] \;, \tag{1.4}$$

with

$$V(T,\vec{\mathrm{H}}_1) = e^{i\hbar^{-1}\mathcal{H}_0 T}\,e^{-i\hbar^{-1}\mathcal{H}T} \;. \tag{1.5}$$

The relaxation equation for the polarization $\langle\vec{\mathrm{S}}\rangle$ in the interaction representation is readily obtained:

$$\frac{d}{dt}\langle\tilde{\mathrm{S}}\rangle = \mathrm{Tr}\left(\frac{\partial\tilde{\rho}}{\partial t}\,\vec{\mathrm{S}}\right)$$
$$= -\frac{1}{T_f}\,[\langle\tilde{\mathrm{S}}\rangle - \mathrm{Tr}\langle V^{\dagger}(T,\vec{\mathrm{H}}_1)\,\vec{\mathrm{S}}\,V(T,\vec{\mathrm{H}}_1)\,\tilde{\rho}(t)\rangle_{\mathrm{av}}] \;. \tag{1.6}$$

Noting that $V(T,\vec{\mathrm{H}}_1)$ is the unitary operator associated with a well-defined rotation $R(T,\vec{\mathrm{H}}_1,\gamma_S)$, the product of a rotation around $\vec{\mathrm{H}}_0+\vec{\mathrm{H}}_1$ by a rotation around $\vec{\mathrm{H}}_0$, we can rewrite the relaxation equation:

$$\frac{d}{dt}\langle\tilde{\mathrm{S}}_i\rangle = -\frac{1}{T_f}\,[\delta_{ij} - \langle R_{ij}(T,\vec{\mathrm{H}}_1,\gamma_S)\rangle_{\mathrm{av}}]\langle\tilde{\mathrm{S}}_j\rangle \;. \tag{1.7}$$

It is in fact more convenient to use spherical components for which the relaxation equation is diagonal. Indeed, the off-diagonal matrix elements of R vanish in this basis when they are averaged over the azimuthal angle ϕ of $\vec{\mathrm{H}}$. The final result is then

$$\frac{d}{dt}\langle\tilde{S}_q\rangle = -\frac{1}{T_f}[1 - \langle R_{q,q}(T,\vec{\mathrm{H}}_1,\gamma_S)\rangle_{\mathrm{av}}]\langle\tilde{S}_q\rangle \;, \tag{1.8}$$

where $q = 0, \pm 1$ and $R_{q,q}$ are the spherical components of R.

We would like to point out that the above derivation is valid for any value of $\vec{\mathrm{S}}^2 = S(S+1)$, provided one uses the correct value of γ_S, and can be readily extended to any irreducible polarization tensor,[6] $\langle T^k_q\rangle$ with $0 \leqslant k \leqslant 2S$:

$$\frac{d}{dt}\langle\tilde{T}^k_q\rangle = -\frac{1}{T_f}\,\{1 - \langle\mathfrak{D}^{\,k}_{qq}[R(T,\vec{\mathrm{H}}_1,\gamma_S)]\rangle_{\mathrm{av}}\}\langle\tilde{T}^k_q\rangle \;, \tag{1.9}$$

where $\mathfrak{D}^k_{qq'}(R)$ is the unitary matrix associated with R, belonging to the irreducible $(2k+1)$-dimension representation of the rotation group.

Let us derive a more explicit expression for the line shift $\delta\omega$ and transverse relaxation time T_2. The time evolution of the transverse polarization $\langle S_\pm\rangle$ is given in terms of T_2 and $\delta\omega$ in the laboratory frame by

$$\frac{d}{dt}\langle S_\pm\rangle = -\left[\frac{1}{T_2} \pm i\,(\delta\omega + \omega_0)\right]\langle S_\pm\rangle \;, \tag{1.10}$$

where

$$\hbar\omega_0 = \gamma_S H_0 \,.$$

Using Eq. (1.8) one immediately finds

$$1/T_2 + i\delta\omega = (1/T_f)\,[1 - \langle R_{+1,+1}(T,\vec{\mathrm{H}}_1,\gamma_S)\rangle_{\mathrm{av}}]$$
$$= (1/T_f)\,[1 - \langle R^{*}_{-1,-1}(T,\vec{\mathrm{H}}_1,\gamma_S)\rangle_{\mathrm{av}}] \;. \tag{1.11}$$

The explicit evaluation of T_2 and $\delta\omega$ are most easily performed in the spin-$\frac{1}{2}$ case; nevertheless, the results are valid for any value of S. In the general case, $\delta\omega$ is the shift of the line associated with the transitions $|\Delta S_z| = 1$. We give below the result obtained when the average over T has been performed explicitly:

$$\frac{1}{T_2} + i\delta\omega = \frac{1}{T_f}\left[1 - \left\langle \left(\sin^4\frac{\alpha}{2}\right)\frac{1}{1 - i(\omega_0+\omega)\,\tau} + \left(\cos^4\frac{\alpha}{2}\right)\frac{1}{1 - i(\omega_0-\omega)\,\tau} + \left(\tfrac{1}{2}\sin^2\alpha\right)\frac{1}{1 - i\omega_0\tau}\right\rangle_{\mathrm{av}}\right] \;, \tag{1.12}$$

where $\hbar\omega = \gamma_S H$, τ is the mean life of the molecular state, and α the angle between $\vec{\mathrm{H}}_0$ and $\vec{\mathrm{H}} = \vec{\mathrm{H}}_0 + \vec{\mathrm{H}}_1$. The average over the direction of $\vec{\mathrm{H}}_1$ can still be performed analytically, but the average over the magnitude of $\vec{\mathrm{H}}_1$, $\hbar\omega_1/\gamma_S$, has to be done by numerical methods. The results are expressed in terms of $\omega_1^* = (\langle\omega_1^2\rangle_{\mathrm{av}})^{1/2}$ or $H_1^* = \hbar\omega_1^*/\gamma_S$.

In the derivation leading to Eq. (1.12), the orbital momentum $\vec{\mathrm{N}}$ has been treated as a classical vector which stays fixed during the lifetime. A more rigorous quantum treatment, similar to that given in Appendix A of Ref. 1, gives the result of Eq. (1.12) provided $N \gg 1$.

Let us now indicate how the above results have to be modified to take into account the nuclear spin I of the alkali atom. We shall assume that the dc field H_0 is small enough so that the Zeeman splitting remains much smaller than the hyperfine structure. Moreover, in all practical cases the spin-orbit coupling $\gamma_S \times \vec{\mathrm{S}}\cdot\vec{\mathrm{H}}_1$ is weak compared to the hyperfine interaction. Finally, in the pressure range of interest the lifetime of the molecular states remains very long compared to the reciprocal of the hyperfine frequency (the inequality $\Delta W\tau \gg 1$ holds at pressures up to several atmospheres). The different conditions stated above imply that an alkali atom, free or bound, stays in a stationary state of the hyperfine Hamiltonian.

In particular, the condition $\Delta W\tau \gg 1$ inhibits "sticking" collision relaxation between two different hyperfine states. We may say that we have to deal with two classes of atoms having different angular momentum, $F_+ = I + \frac{1}{2}$ and $F_- = I - \frac{1}{2}$. "Sticking" collisions act independently on the two kinds of atoms without mixing them. We have then simply to apply the above results to atoms of each class, using the following values of ω_0 and ω_1:

$$\omega_0 = \hbar^{-1}\gamma_{F_\pm} H_0 = \pm \hbar^{-1}\gamma_S H_0/(2I+1) \ ,$$

$$\omega_1 = \pm \hbar^{-1}\gamma N/(2I+1) \ ,$$

the upper and lower signs holding for each class.

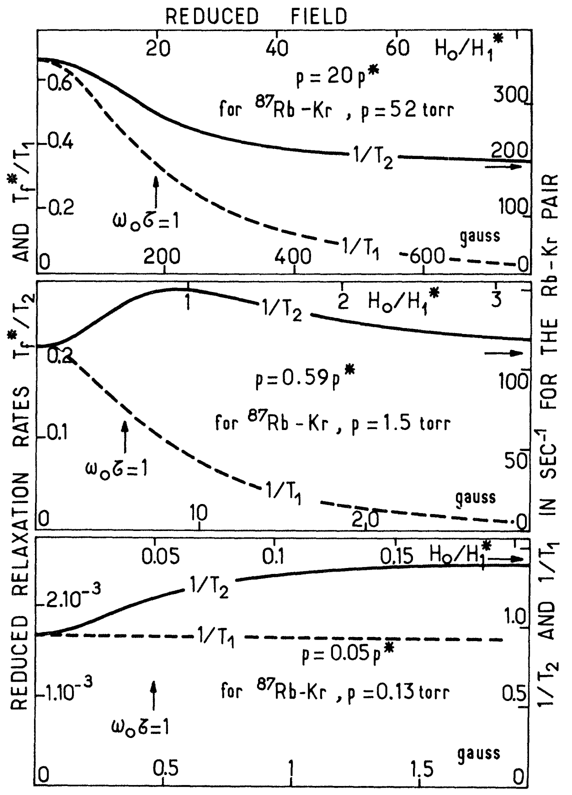

FIG. 1. Longitudinal and transverse relaxation rates $1/T_1$ and $1/T_2$ induced by "sticking" collisions, computed versus the magnetic field H_0, for an alkali-rare-gas mixture, at three different pressures. (At the lowest pressure the decrease of $1/T_1$ around H_1^* described in Ref. 1, is not apparent with our scale.) All physical quantities are expressed in reduced units defined in the text. The scales are also indicated in current units for one typical case, corresponding to the Rb-Kr pair.

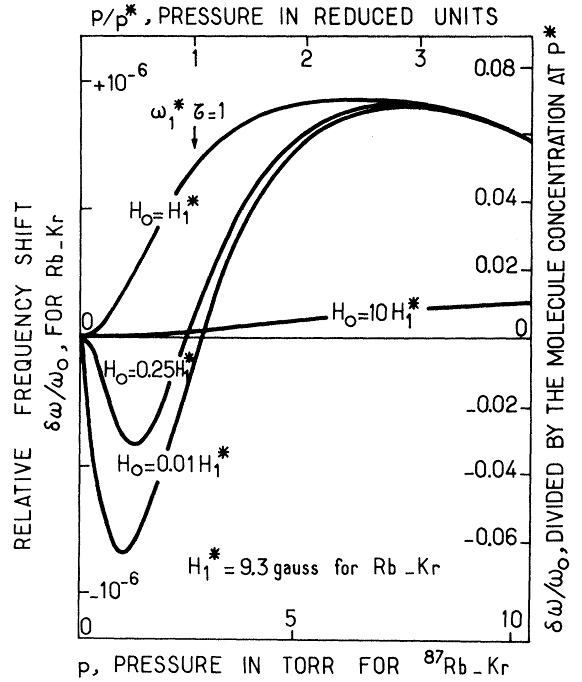

FIG. 2. Relative Zeeman frequency shift $\delta\omega/\omega_0$, induced by "sticking" collisions, computed versus the pressure, for an alkali–rare-gas mixture, in four different fields. The pressure and the field are expressed in reduced units and $\delta\omega/\omega_0$ is divided by the molecule concentration at $P = P^*$. The scales are also indicated in the case of the Rb-Kr pair.

We would like to make some comments on the remarkable features of the variations of T_2 and $\delta\omega$ with the static magnetic field and the rare-gas pressure, as illustrated by the curves of Figs. 1–3. To allow one to use these curves for different alkali–rare-gas pairs, we have introduced reduced coordinates. The magnetic field is expressed in units of H_1^* (the root-mean-square value of the effective magnetic field simulating the spin-orbit interaction), the pressure is expressed in units of p^*, the pressure at which the mean molecular lifetime τ satisfies the condition $\omega_1^*\tau = 1$, and the relaxation rate is in units of the molecule formation rate $1/T_f^*$ at the pressure p^*. We have also drawn the scales in current units for one typical case (that of the Rb-Kr pair).

Let us discuss first the transverse relaxation time T_2. In the limit of zero magnetic field, the spherical symmetry of the problem implies $T_2 = T_1$. We refer the reader to Ref. 1, Sec. V D, where the variation in $T_1 = T_2$ with the gas pressure is thoroughly discussed. In Fig. 1, we see that the variation of $1/T_2$ with H_0 differs markedly from that of $1/T_1$ (always looking like a decreasing Lorentzian curve) when the rare-gas pressure is sufficiently low that the lifetime τ of the molecular state satisfies the inequality $\omega_1^*\tau \gg 1$. The increase of $1/T_2$ with the dc field H_0 in this pressure range can be understood in a rather simple way. When $\omega_0 \ll \omega_1$, there is a class of bound

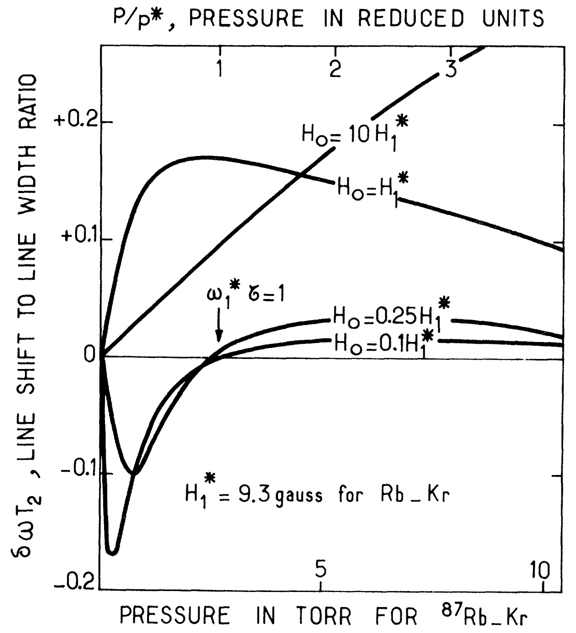

FIG. 3. Line shift to linewidth ratio, $\delta\omega T_2$, for the relaxation induced by "sticking" collisions, computed versus the pressure for an alkali–rare-gas mixture, in four different magnetic fields. The pressure and the field are expressed in the reduced units P^* and H_1^*, defined in the text. The scales are also indicated in current units for the specific case of the Rb-Kr pair.

atoms for which $\langle\vec{S}\rangle$ is nearly blocked, those for which $\vec{N}$ makes a small angle with respect to $\langle\vec{S}\rangle$. The phase shift of $\langle S_\pm\rangle$ between these atoms and the free ones ($\sim\omega_0\tau$) is clearly an increasing function of the dc field H_0. When H_0 becomes much larger than the effective field, the bound alkali atoms remain in eigenstates of S_z ($T_1\to\infty$) but still suffer random phase shifts given by $\hbar^{-1}\gamma N_z T$ and much larger than π (since $\omega_1^*\tau\gg1$). In this limit $1/T_2$ keeps a constant value given by $1/T_f$. We remark also in this low-pressure range, that the parameters governing the shapes of the curves are different: H_1^* for $1/T_1$, τ for $1/T_2$; it follows that the experimental study of T_1 and T_2 will yield complementary information.

In a practical situation, one must, of course, also take into account the existence of a relaxation rate linear in pressure due to two-body collisions ("sudden" collisions). Since $1/T_2$ induced by "sticking" collisions is pressure independent at sufficiently high pressures, there is always a pressure range where the effect of "sudden" collisions becomes dominant. (In the case of a Rb-Kr mixture, the "sudden" and the "sticking" collisions should give effects of the same order of magnitude at a pressure of 20 Torr.)

Let us now turn our attention to the line shift $\delta\omega$. The variations of $\delta\omega/\omega_0$ and $\delta\omega T_2$ with the pressure are displayed in Figs. 2 and 3 for different values of the ratio $\omega_0/\omega_1^*=H_0/H_1^*$. In order to collect results which are valid for several alkali-rare-gas pairs in a single diagram, we have plotted in Fig. 2 the ratio between $\delta\omega/\omega_0$ and the concentration C_b^* of bound alkali atoms at the pressure p^*. (This number is given in Ref. 1 for the Rb-Kr pair.) We note first, that $\delta\omega/\omega_0$ may take appreciable values, of the order of 10^{-6}, much larger than those predicted by Herman[3] (a more detailed comparison is given below. The product $\delta\omega T_2$, which, as we shall see later, usually gives the ratio between the shift and the half-width of the Zeeman resonance line, is of the order of unity under various conditions, allowing an experimental determination of $\delta\omega$ with a reasonable signal-to-noise ratio. A striking feature of the variation of $\delta\omega/\omega_0$ with the pressure is the change of its sign which occurs at a pressure such that $\omega_1^*\tau\sim1$ when the effective field $|\vec{H}_1|$ is larger than the static field. The negative value of the shift in the low-magnetic-field pressure range can be understood in the following way. The lifetime of the molecule is long enough so that it behaves like a stationary system in an eigenstate of $\vec{S}\cdot\vec{N}$, since $\gamma_S\vec{S}\cdot\vec{H}_1\gg\gamma_S\vec{S}\cdot\vec{H}_0$. The Landé factor of an atom bound in a molecule, given by $g_S/(2N+1)$ is considerably smaller than that of the free atom g_S. It is not surprising then, to get for $\delta\omega/\omega_0$ a negative value of the order of C_b, the ratio between the numbers of bound and free alkali atoms. On the other hand, when the lifetime of the molecule is very short, the atom remains approximately in an eigenstate of $\gamma_S\vec{S}\cdot\vec{H}_0$. The shift can be computed using the general result of second-order perturbation theory for a two-level system, which always leads to a positive frequency shift. Furthermore, when the rare-gas pressure is increased, the decrease of the shift associated with an individual "sticking" collision is partly counterbalanced by the fast increase in the collision rate. For high static fields $|\vec{H}_0|\gg|\vec{H}_1|$, second-order perturbation theory can be used in the whole pressure range so that the shift is always positive.

To conclude, we would like to discuss briefly mechanisms leading to a shift of the Zeeman resonance line, other than those dealt with in the present paper. First, we would like to consider the effect of the spin-orbit coupling in two-body collisions ("sudden" collisions). Time-dependent perturbation theory is always valid in this case and the calculated fractional shift is found to be of the order of $(\tau_{\text{coll}}/\tau_f)(\omega_1\tau_{\text{coll}})^2$ (τ_{coll} is the collision duration and τ_f the time of flight), a value completely negligible with respect to the effect of "sticking" collisions. Instead of looking to higherorder effects of the spin-orbit coupling, as we have done here, Herman[3] has recently studied the effect of an interaction between an alkali–rare-gas pair in the presence of a magnetic field, of the following form:

$$\gamma_S\left[g_0(r)\,\vec{S}\cdot\vec{H}_0+g_2(r)\left(\frac{(\vec{S}\cdot\vec{r})\,(\vec{H}_0\cdot\vec{r})}{r_2}-\tfrac{1}{3}\vec{S}\cdot\vec{H}_0\right)\right] \quad ,$$

where $\vec{r}$ is the interatomic distance. Herman was able to relate $g_0(r)$ and $g_2(r)$ to the spin-orbit potential $\gamma(r)$

$$g_0(r)=-\tfrac{2}{9}\,\gamma(r)\,\mu r^2/\hbar^2=-\tfrac{2}{3}\,g_2(r) \quad ,$$

where μ is the reduced mass. As shown by Herman, it is a very simple matter to estimate the fractional shift $\delta\omega/\omega_0$ from the longitudinal-relaxation analysis. The results in a typical case are given in Table I both for the "sticking" and "sudden" collisions and compared with our present findings. One sees clearly that the shift computed in the present work can, in the pressure range of a few Torr, be larger than the effect calculated by Herman by several orders of magnitude. However we should stress the fact, not apparent enough in Fig. 2, that, at sufficiently high pressures ($\omega_0\tau$, $\omega_1^*\tau \ll 1$), the shift induced by "sticking" collisions (then very weak) behaves always as a decreasing function of the pressure. For instance, at 1 atm, our predicted $\delta\omega/\omega_0$ becomes as small as 10^{-11} for the Rb-Kr pair, and is less than Herman's.

As a final remark we shall say a few words about the case of muonium (bound state between a μ^+ meson and an electron). This system is usually produced and studied in a rare-gas medium (argon) at a pressure of several atmospheres.[4] We would like to show that the effects due to "sticking" collisions play a negligible role. For a given well depth the total number of bound states is roughly proportional to $\mu^{3/2}$ (μ is the reduced mass).[7] This number will pass from a few thousands for the argon-Rb pair to a few units for the muonium-argon one, assuming the same potential depth in both cases. (For a given rare-gas atom, this quantity does not change very much with the alkali atom.[8]) The fraction of bound alkali atoms depends very little on the reduced mass μ since the phase space for the free particles is also proportional to $\mu^{3/2}$. But the bound states of the muonium-argon pair, if there are any, will have very low orbital angular momenta N (few units of $\hbar$), while the average $\bar{N}\hbar$ is around $25\hbar$ for the Rb-argon pair. Since $\delta\omega/\omega_0$ is roughly proportional to the square of the spin-orbit strength, one loses automatically a factor of 10^{-2}–10^{-3}. Furthermore, the experiments were conducted with quite high pressures (a few atmospheres), where the effect of "sticking" collisions is very small even in the most favorable cases.

TABLE I. Relative Zeeman-frequency pressure shift $\delta\omega/\omega_0$. Computed values of the shift induced by two different interactions and two different types of collisions for the Rb–Kr pair at a Kr pressure P of 1 and 10 Torr.

P (Torr)	$\delta\omega/\omega_0$	"sticking" collisions	"sudden" collisions
1	Herman's	$\approx -10^{-9}$	$\approx -6\times10^{-9}$
	Present work	$-8\times10^{-7\,a}$	$2\times10^{-12\,a}$
10	Herman's	$\approx -10^{-8}$	$\approx -6\times10^{-8}$
	Present Work	8×10^{-7}	$2\times10^{-11\,a}$

[a] Value which depends on ω_0 and ω_1^* and is indicated here for the case $\omega_0 \ll \omega_1^*$.

Similar remarks are also valid for the relaxation of an alkali in the presence of a light rare gas (helium and neon). In this case, the "sticking" collisions play a negligible role.

II. EFFECTS PRODUCED BY "STICKING" COLLISIONS ON EVOLUTION OF HYPERFINE "COHERENCES"

We shall first discuss the effect of the spin-orbit interaction and then of the isotropic hyperfine interaction which plays a very important role here. Finally, we shall compare the theoretical predictions to available experimental results.

A. Spin-Orbit Interaction

We shall assume that the rare-gas pressure is such that the average lifetime τ of the molecular state satisfies the condition $\Delta W\tau \gg 1$, where ΔW is the hyperfine splitting. The evolution operator can be shown (see Sec. I) to reduce to a tensor product

$$\mathcal{U}=\mathcal{U}_+\otimes\mathcal{U}_- \quad , \tag{2.1}$$

where $\mathcal{U}_\pm$ are acting, respectively, in the subspaces $F_\pm = I\pm\frac{1}{2}$. We want to study the evolution of hyperfine "coherences," the off-diagonal density-matrix elements such that

$$C_{m,n}(t)=\langle F_+ m\,|\rho(t)|\,F_- n\rangle \quad , \tag{2.2}$$

m and n being two eigenvalues of F_z. We shall work in the interaction representation with respect to the free-atom Hamiltonian. Noting that the Larmor frequencies in the two hyperfine states are nearly opposite $\omega_{F_+}\simeq-\omega_{F_-}=\omega_0$, we have

$$C_{m,n}(t)=e^{-i[\Delta W+\omega_0(m+n)]t}\,\tilde{C}_{m,n}(t) \quad . \tag{2.3}$$

For the free atoms $\tilde{C}_{m,n}$ is time independent.

We follow the same type of reasoning as in Sec. I. For the atom of class (a), the $\tilde{C}_{m,n}$ at time $t+\Delta t$ are given in terms of the $\tilde{C}_{m'n'}$ at time t by

$$\tilde{C}_{m,n}(t+\Delta t)=\sum_{m',n'}\langle\langle F_+ m\,|\tilde{\mathfrak{U}}_+|F_+ m'\rangle$$
$$\times\langle F_- n'\,|\tilde{\mathfrak{U}}_-^\dagger|\,F_- n\rangle\rangle_{\text{av}}\tilde{C}_{m',n'}(t)\quad,\qquad(2.4)$$

where $\tilde{\mathfrak{U}}_\pm(t_0, T, \vec{\text{H}}_1)$ are obtained from Eq. (1.2) by inserting the correct Larmor frequency for each hyperfine state. Let us exhibit the dependence of the right-hand side of the above equation upon ϕ, the azimuthal angle of the effective magnetic field $\vec{\text{H}}$ and perform the corresponding average:

$$\langle e^{i(m'-m-n'+n)\phi}\rangle=\delta_{m-n,m'-n'}\quad.\qquad(2.5)$$

The evolution equation will be written in terms of the operators $V_\pm(T, \vec{\text{H}}_1)$, relative to the two hyperfine subspaces [deduced from Eq. (1.5) by inserting the correct Larmor frequency for each one]. The density-matrix element $\tilde{C}_{m,n}$ for the whole ensemble is given at the instant $t+\Delta t$ by

$$\tilde{C}_{m,n}(t+\Delta t)=(1-\Delta t/T_f)\,\tilde{C}_{m,n}(t)$$
$$+\sum_q e^{2i\omega_0 q t_0}\langle m\,|V_+|m+q\rangle$$
$$\times\langle n+q\,|V_-^\dagger|n\rangle\,\tilde{C}_{m+q,n+q}(t)\quad.\qquad(2.6)$$

Note that the instant t_0 does not disappear; this is due to the fact that the Larmor frequencies are opposite in the two hyperfine states.

Before we can write down a relaxation equation for the $\tilde{C}_{m,n}(t)$, a careful discussion is needed. We shall consider two cases.

(i) $\omega_0 T_f \lesssim 1$. The dc magnetic field is small enough (or the pressure large enough) so that the Larmor frequency ω_0 is of the order or smaller than the molecular formation rate. Since Δt is chosen such that $\Delta t \ll T_f$, we necessarily have $\omega_0\Delta t\ll 1$. It is then legitimate to replace t_0 by t in the exponential $e^{2i\omega_0(m-m')t_0}$. The $\tilde{C}_{m,n}(t)$ obey a system of coupled differential equations:

$$\frac{d\tilde{C}_{m,n}}{dt}=\frac{1}{T_f}\Big[\sum_q e^{2iq\omega_0 t}\langle\langle m\,|V_+\,|m+q\rangle$$
$$\times\langle n+q\,|V_-^\dagger|n\rangle\rangle_{\text{av}}\tilde{C}_{m+q,n+q}(t)-\tilde{C}_{m,n}(t)\Big]\quad.\qquad(2.7)$$

Using only the unitarity of the matrices $V_\pm$, it is possible to show that the oscillating coupling terms $(q\neq 0)$ do contribute only if $\omega_0 T_{m,n}\lesssim 1$, where $T_{m,n}$ is the relaxation time of $\tilde{C}_{m,n}$ in the absence of the coupling terms ($T_{m,n}$ is much larger than T_f when the motion-narrowing condition $\omega_1^*\tau\ll 1$ is satisfied).

(ii) $\omega_0 T_f\gg 1$. This case corresponds to a low pressure or a high dc field situation where the Larmor frequency is much larger than the molecular formation rate. We have to distinguish two subcases.

(a) $\omega_0\tau\geq 1$. Since Δt must be chosen such that $\Delta t\gg\tau$, we have $\omega_0\Delta t\gg 1$. The average over t_0 in the interval $(t, t+\Delta t)$ gives zero unless $m=m'$:

$$\langle e^{2i\omega_0(m-m')t_0}\rangle=\delta_{m,m'}\quad.$$

The $\tilde{C}_{m,n}$ satisfy decoupled differential equations.

(b) $\omega_0\tau\ll 1$. Here, depending on the exact value of ω_0, we may have to choose either $\omega_0\Delta t\gg 1$ or $\omega_0\Delta t\ll 1$ in order to write a differential equation. But since the condition $\omega_0 T_{m,n}\gg 1$ is always satisfied $(T_{m,n}\geq T_f)$, even if the coupling terms appear explicitly in the differential equations, they do not contribute, so the result is independent of the choice of Δt.

To conclude this discussion we can say that the $\tilde{C}_{m,n}$ will obey the decoupled relaxation equations given below provided the Larmor frequency is larger than the relaxation rate $T_{m,n}^{-1}$. Experimentally this situation will be realized, at least approximately, when the transition lines $F_+ m \rightleftharpoons F_- n$ corresponding to different values of F_z are resolved (remember that the linewidth is larger or equal to $T_{m,n}^{-1}$):

$$\frac{d\tilde{C}_{m,n}}{dt}=\frac{1}{T_f}\Big[-1+\langle\langle m|\,V_+(T,\vec{\text{H}}_1)\,|m\rangle$$
$$\times\langle n\,|\,V_-^\dagger(T,\vec{\text{H}}_1)\,|n\rangle\rangle_{\text{av}}\Big]\tilde{C}_{m,n}(t)$$
$$=\Big[-(1/T_{m,n})_{\text{SO}}+i\,\delta\omega_{m,n}\Big]\tilde{C}_{m,n}(t)\quad,\qquad(2.8)$$

where

$$V_\pm(T,\vec{\text{H}}_1)=e^{i\hbar^{-1}\mathcal{H}_0^\pm T}e^{-i\hbar^{-1}\mathcal{H}^\pm T}\quad,\qquad(2.9)$$

with

$$\mathcal{H}_0^\pm=\gamma_{F_\pm}\vec{\text{F}}^\pm\cdot\vec{\text{H}}_0\;,\quad \mathcal{H}^\pm=\gamma_{F_\pm}\vec{\text{F}}^\pm\cdot(\vec{\text{H}}_0+\vec{\text{H}}_1)\quad.\qquad(2.10)$$

Using the properties of the rotation matrices, one can prove that $\delta\omega_{m,n}$ is present only if $m+n\neq 0$. This shift of the transition line $F_+ m\rightleftharpoons F_- n$ is related to the Zeeman level shift studied previously and cannot be interpreted as a shift of the hyperfine levels since the frequency of the hyperfine transition $F_+ 0\rightleftharpoons F_- 0$ is not affected.

We shall give a more explicit expression for $T_{0,0}$ in the case of the transition $F_+, 0\rightleftharpoons F_- 0$:

$$\left(\frac{1}{T_{0,0}}\right)_{\text{SO}}=\frac{1}{T_f}\,[1-\langle P_{F_+}(\cos\eta)P_{F_-}(\cos\eta)\rangle_{\text{av}}]\quad,\qquad(2.11)$$

where $P_l(x)$ is the Legendre polynomial of order

l and

$$\cos\eta = 1 - 2\sin^2\alpha \sin^2(\tfrac{1}{2}\omega T) \quad . \tag{2.12}$$

B. Isotropic Hyperfine Interaction

Let us now deal with the effect of a modification of the hyperfine interaction $\alpha(r)\vec{S}\cdot\vec{I}$, due to the presence of a rare-gas atom at the distance r. Let us call Ω_{vN} the modification of the hyperfine splitting for an alkali atom engaged in a molecular state of vibrational number v and rotational number N:

$$\Omega_{vN} = \tfrac{1}{2}(2I+1)\int \hbar^{-1}\alpha(r)\,|\psi_{vN}(\vec{r})|^2 d^3r \quad , \tag{2.13}$$

where $\psi_{vN}(\vec{r})$ is the wave function of the molecular state. We shall neglect the dispersion of the values of Ω_{vN} and assume the same $\Omega = \langle\Omega_{vN}\rangle_{\text{av}}$ for all the molecular states.

With the same reasoning as above, we arrive immediately at the relaxation equation for $\tilde{C}_{m,n}(t)$ valid if $\Delta W\tau \gg 1$:

$$\frac{d\tilde{C}_{m,n}(t)}{dt} = \frac{1}{T_f}\langle e^{-i\Omega T} - 1\rangle_{\text{av}}\tilde{C}_{m,n}(t) \quad , \tag{2.14}$$

$$\frac{d\tilde{C}_{m,n}(t)}{dt} = -\left[\left(\frac{1}{T_{m,n}}\right)_{\text{hf}} + i\delta W\right]\tilde{C}_{m,n}(t) \quad . \tag{2.15}$$

Performing the average over T we get the simple expressions

$$\left(\frac{1}{T_{m,n}}\right)_{\text{hf}} = \frac{1}{T_f}\,\frac{\Omega^2\tau^2}{1+\Omega^2\tau^2} \,, \quad \delta W = \frac{1}{T_f}\,\frac{\Omega\tau}{1+\Omega^2\tau^2} \,. \tag{2.16}$$

Before we apply these formulas to actual physical situations, let us briefly discuss the effect of the hyperfine interaction induced during "sudden" two-body collisions. We follow closely the analysis of Ref. 1, Sec. IV. A two-body collision is characterized by the impact parameter $\vec{b}$, the relative velocity $\vec{V}$ of the two colliding atoms, and the instant t_c when the distance $r(t)$ between the two atoms reaches its minimum. The actual motion will be approximately represented by that of two colliding hard spheres of radius $\frac{1}{2}r_0$. To the lowest order of perturbation theory, the transverse relaxation time and the line shift will be given in terms of averages of the phase shift $\phi(\vec{b}, \vec{V})$ corresponding to individual $(\vec{b}, \vec{V}, t_c)$ collisions:

$$\phi(\vec{b}, \vec{V}) = \tfrac{1}{2}(2I+1)\int_{-\infty}^{+\infty}\hbar^{-1}\alpha[r(t-t_c, \vec{b}, \vec{V}]\,dt \quad . \tag{2.17}$$

The actual expressions for T_2 and δW read as follows:

$$1/T_2 = \tfrac{1}{2}(\langle\phi^2\rangle_{\text{av}}/\tau_f), \quad \delta W = \langle\phi\rangle_{\text{av}}/\tau_f \quad . \tag{2.18}$$

The average time of flight is defined as $\tau_f = (\pi r_0^2 \overline{V}_r \mathcal{V}^{-1} N_G)^{-1}$, $\overline{V}_r$ being the mean relative velocity and $N_G\mathcal{V}^{-1}$ the gas number density. The averaged ϕ^n is given by

$$\langle\phi^n\rangle_{\text{av}} = \tau_f \int [\phi(\vec{b}, \vec{V})]^n d^2b\, V n(\vec{V})\, d^3V \quad , \tag{2.19}$$

where $n(\vec{V})$ is the thermal distribution of relative velocities. It will be convenient for later discussions to write $\langle\phi^n\rangle_{\text{av}}$ in terms of Ω:

$$\langle\phi^n\rangle_{\text{av}} = \lambda_n(\Omega\tau_{\text{coll}})^n \quad , \tag{2.20}$$

with the collision time τ_{coll} defined as $\tau_{\text{coll}} = r_0/\overline{V}_r$. The average interaction is of the same order of magnitude for a "sudden" and a "sticking" collision. So λ_n is a dimensionless parameter expected to be of the order of unity, depending mainly on the shape of the function $\alpha(r)$.

C. Comparison of Theoretical Predictions with Available Experimental Results

(i) The relaxation time associated with the off-diagonal matrix element $\tilde{C}_{00}(t) = \langle 2\ 0|\tilde{\rho}(t)|1\ 0\rangle$ for ^{87}Rb atoms has been studied experimentally by Bender and Cohen,[5] in an uncoated cell containing a foreign gas. The field was chosen so that the different hyperfine lines were resolved: $\omega_0 T_{0,0} > 1$. They have found, with argon as a foreign gas, that it is not possible to account for the experimental results concerning $T_{0,0}$ only in terms of wall relaxation after diffusion through the gas, and relaxation by binary collisions between Rb and argon atoms ("sudden" collisions). It appears necessary to invoke a third almost pressure-independent relaxation mechanism giving a broadening of 15 cycles which corresponds to a $(T_{0,0})^{-1}$ of 47 sec^{-1}. Bender[5] has suggested that the "sticking" collisions analyzed in Ref. 1 might explain this new effect. We would like to show that it is indeed the case. Let us consider first the effect of the spin-orbit coupling. Using Eq. (2.11), we have

$$\left(\frac{1}{T_{0,0}}\right)_{\text{SO}} = \frac{1}{T_f}\left[1 - \langle\tfrac{1}{2}\cos\eta\,(3\cos^2\eta - 1)\rangle_{\text{av}}\right] \quad . \tag{2.21}$$

In the range of pressures explored, $\omega\tau \ll 1$. The steady magnetic field was such that $H_0 \ll H_1$. We have then

$$\cos\eta \simeq 1 - \tfrac{1}{2}\omega_1^2 T^2 \sin^2\theta \quad , \tag{2.22}$$

where θ is the angle between $\vec{H}_0$ and $\vec{H}_1$. Keeping only the lowest-order term in $(\omega_1 T)^2$ we get

$$\begin{aligned}(1/T_{0,0})_{\text{SO}} &= (2/T_f)\langle\omega_1^2 T^2 \sin^2\theta\rangle_{\text{av}} \\ &= (8/3T_f)\,\omega_1^{*2}\tau^2 = (4/T_1)_{\text{SO}} \quad .\end{aligned} \tag{2.23}$$

We note first that since T_f^{-1} is proportional to the square of the pressure, the above expression is indeed pressure independent. Using recent experimental results concerning the longitudinal relaxation in the Rb-A mixture,[9] we obtain

$$(1/T_{0,0})_{\text{SO}} = 8.6 \text{ sec}^{-1} \quad . \tag{2.24}$$

On the other hand the contribution of the hyperfine interaction (assuming for the moment $|\Omega|\tau \ll 1$) is obtained from Eq. (2.16):

$$(1/T_{0,0})_{\mathrm{hf}} \simeq (1/T_f)\,\Omega^2\tau^2 \qquad (2.25)$$

and is also pressure independent.

To have an idea of the order of magnitude of Ω, we use the experimental results about the hyperfine pressure shift measured near room temperature[10]:

$$\delta W = \frac{\langle\phi\rangle_{\mathrm{av}}}{\tau_f} = \lambda_1\,\Omega\,\frac{\tau_{\mathrm{coll}}}{\tau_f} = -\,7.5\times10^{-9}\,\Delta W\ \mathrm{Torr}^{-1}\ . \qquad (2.26)$$

Using $\tau_{\mathrm{coll}}/\tau_f = 10^{-5}$ Torr^{-1}, $\tau = 5\times10^{-8}$ sec/Torr^{-1}, and $T_f = 4.3\ 10^2$ sec/Torr^2,[9] one can check that the condition $|\Omega|\tau < 1$ is satisfied in the range of observation. The total effect of "sticking" collisions on $(T_{0,0})^{-1}$ is finally given in terms of the dimensionless constant λ_1, as

$$(1/T_{0,0})_{\mathrm{SO}} + (1/T_{0,0})_{\mathrm{hf}} = \left(8.6 + \frac{102}{\lambda_1^2}\right)\ \mathrm{sec}^{-1}\ . \qquad (2.27)$$

The result of Bender is reproduced if one takes $\lambda_1 = 1.6$, which looks quite reasonable.

(ii) The shift of the hyperfine transition line in ^{87}Rb due to collisions with argon atoms has been studied by Ensberg and zu Putlitz[11] at high argon pressure (about 5 and 10 atm). They found evidence for a nonlinear pressure dependence of the shift δW. Their results have been fitted with the following empirical formula:

$$\delta W/\Delta W = ap + bp^2\ , \qquad (2.28)$$

with $ap\ \Delta W = -\,330$ kc/sec, $bp^2\,\Delta W = 11$ kc/sec at $p = 4170$ Torr (at this pressure the linewidth is 3 kc/sec.

"Sticking" collisions can produce a contribution to the hyperfine shift with a nonlinear pressure dependence [see Eq. (2.16)]. However, this contribution to the line shift is predicted to be smaller than the corresponding line broadening in the pressure range where a nonlinear behavior appears. Since the nonlinear term in the above empirical formula (2.28) turns out to be larger than the observed linewidth, "sticking" collisions cannot account for it. In fact, even the sign is not correctly reproduced. The explanation of the effect observed by Ensberg and zu Putlitz is probably to be found in more complicated three-body effects than those considered in this paper.

III. EFFECT OF rf FIELD ON RELAXATION INDUCED BY "STICKING" COLLISIONS

We would like to study the evolution of an ensemble of alkali atoms in a rare gas in the presence of a rf field, of frequency ω', when the "sticking" collisions leading to alkali–rare-gas molecules are the dominant relaxation mechanism. Interesting effects are expected to appear when the amplitude $H'_1 = |\hbar\omega'_1/\gamma_F|$ of the rf field is such that $\omega'_1\tau \gtrsim 1$, where τ is the average lifetime of the molecular states. In particular, we shall see that it is possible to induce transitions between Zeeman levels of the molecules at frequencies characteristic of the molecular fine structure due to the $\vec{S}\cdot\vec{N}$ coupling, and well separated from the resonance frequency $\omega_0/2\pi$ of the free atoms. These transitions could be detected by their effects on the relaxation rates. On the other hand, when the condition $\omega'_1\tau \ll 1$ is satisfied, the relaxation process is not affected by a rf field such that $\omega' \simeq \omega_0$, and the Bloch equations will be shown to be valid. We shall first deal with this latter case.

A. Derivation of Bloch Equations

We define $\mathcal{H}_f(t)$ as the total Hamiltonian of the free atoms

$$\mathcal{H}_f(t) = \mathcal{H}_0 + \mathcal{H}'_1(t)\ , \qquad (3.1)$$

where $\mathcal{H}_0 = \gamma_S\,\vec{S}\cdot\vec{H}_0$ and $\mathcal{H}'_1(t)$ is the Hamiltonian associated with the rf field

$$\mathcal{H}'_1(t) = \gamma_S\,\vec{S}\cdot\vec{H}'_1(t) = \hbar\omega'_1\,(S_+e^{-i\omega' t} + S_-e^{i\omega' t})\ ,$$

and $\mathcal{H}_b(t)$ as the total Hamiltonian of the bound atoms

$$\mathcal{H}_b(t) = \mathcal{H}_f(t) + \mathcal{H}_1\ , \qquad (3.2)$$

with $\mathcal{H}_1 = \gamma_S\,\vec{S}\cdot\vec{H}_1$. It is convenient to transform the density matrix $\rho(t)$ into the rotating frame:

$$\bar{\rho}(t) = e^{iS_z\omega' t}\rho(t)\,e^{-iS_z\omega' t}\ . \qquad (3.3)$$

In this frame the Hamiltonian $\bar{\mathcal{H}}_f$ governing the evolution of the free atom is

$$\bar{\mathcal{H}}_f = \hbar(\omega_0 - \omega')S_z + \hbar\omega'_1 S_x\ . \qquad (3.4)$$

We shall assume that $\omega_0 - \omega'$ is of the order of ω'_1. Let us choose a time interval Δt satisfying the three conditions

$$\Delta t/T_f \ll 1,\quad \omega'_1\,\Delta t \ll 1,\quad \Delta t/\tau \gg 1\ . \qquad (3.5)$$

The above conditions can be realized simultaneously provided $\omega'_1\tau$ is small enough. Let us compute $\bar{\rho}(t+\Delta t)$ in terms of $\bar{\rho}(t)$, keeping only the first-order term in $\omega'_1\,\Delta t$ and $\Delta t/T_f$. For atoms of class (b) (free atoms), we have

$$\bar{\rho}(t+\Delta t) - \bar{\rho}(t) = i\hbar^{-1}\Delta t\,[\bar{\rho}(t), \bar{\mathcal{H}}_f]\ . \qquad (3.6)$$

For an atom of class (a), the modification of the density matrix in the intervals (t, t_0) and $(t_0 + T, t + \Delta t)$ when the governing Hamiltonian is $\mathcal{H}_f(t)$ are of the order of $\omega'_1\,\Delta t$, but since atoms of class (a) represent only a fraction $\Delta t/T_f$ of the total, the effect on the variation of the density matrix of the whole ensemble will only be of the order of $(\Delta t/T_f)\cdot(\omega'_1\Delta t)$.

We shall assume now that ω' *does not coincide with any of the reasonance frequencies of the bound atom*. This condition will be automatically obtained if $H_1 \gg H_0 > H'_1$. It is then legitimate to ignore the rf field in the interval (t_0, t_0+T) when the atoms are bound. We have: $\mathcal{H}_b(t) \simeq \mathcal{H}_0 + \mathcal{H}_1$. In evaluating $\overline{\mathcal{H}}_b(t) = e^{i\omega' S_z t}\mathcal{H}_b(t)e^{-i\omega' S_z t}$, we can also replace ω' by ω_0. The error in the final result is easily seen to be of the order of $(\omega_0-\omega')\tau \sim \omega'_1\tau \ll 1$. As a conclusion, to compute the difference $\overline{\rho}(t+\Delta t)-\overline{\rho}(t)$ for atoms of class (b) we can ignore the rf field and use the results of Sec. I.

We are now able to write the expression for $\overline{\rho}(t+\Delta t)$ in terms of $\overline{\rho}(t)$ for the whole ensemble in the rotating frame:

$$\overline{\rho}(t+\Delta t) = i\hbar^{-1}\Delta t\,[\overline{\rho}(t), \overline{\mathcal{H}}_f(t)] + \left(1-\frac{\Delta t}{T_f}\right)\overline{\rho}(t) + (\Delta t/T_f) \times [\langle V(T,\vec{\mathrm{H}}_1)\overline{\rho}(t)V^{\dagger}(T,\vec{\mathrm{H}})\rangle_{\mathrm{av}}], \tag{3.7}$$

where terms of the order of $(\Delta t/T_f)$. $(\omega'_1\Delta t)$ have been dropped. From this equation we deduce immediately the Bloch equations for the electronic polarization $\langle\overline{\mathrm{S}}\rangle$ in the rotating frame:

$$\frac{d}{dt}\langle\overline{S}_z\rangle = -\frac{1}{T_1}\langle\overline{S}_z\rangle - i\frac{\omega'_1}{2}(\langle\overline{S}_+\rangle - \langle\overline{S}_-\rangle), \tag{3.8}$$

$$\frac{d}{dt}\langle\overline{S}_\pm\rangle = \left[-\frac{1}{T_2} \pm i(\omega_0+\delta\omega-\omega')\right]\langle\overline{S}_\pm\rangle \mp i\omega'_1\langle\overline{S}_z\rangle, \tag{3.9}$$

where T_1^{-1}, $T_2^{-1} \pm i\delta\omega$ are the relaxation constants calculated in Sec. I. Thus, the resonance line will be represented by a Lorentzian curve centered at $\omega_0+\delta\omega$ and having a half-width $\Delta\omega = (T_2)^{-1}$. In the case for which the motion-narrowing condition is satisfied $(\gamma_S|\vec{\mathrm{H}}_1|\tau \ll 1)$, we recover a general result of the spin-relaxation theory.[12]

B. Relaxation Induced by rf Transitions between Levels of Alkali-Rare-Gas Molecules

We have shown[1] that when the dc magnetic field is strong enough to decouple the electronic spin $\vec{\mathrm{S}}$ and the molecular orbital momentum $\vec{\mathrm{N}}$, "sticking" collisions no longer provide an efficient longitudinal relaxation mechanism. When an alkali atom is engaged in a molecular state, the Zeeman-transition line $\omega' = \omega_0$ is split by the spin-orbit coupling $\gamma\,\vec{\mathrm{S}}\cdot\vec{\mathrm{N}}$ into several lines, falling at $\omega' = \omega_0 + \hbar^{-1}\gamma N_z/(2I+1)$ (N_z is the projection of $\vec{\mathrm{N}}$ along H_0). We would like to show that by applying a rf field of frequency $\omega' \neq \omega_0$ but containing the frequencies $\omega_0 + \hbar^{-1}\gamma N_z/(2I+1)$, it is possible to restore the efficiency of the "sticking" collisions as a relaxation mechanism by inducing transitions $|\Delta F_z| = 1$, $\Delta N_z = 0$, between the Zeeman levels of the bound atoms. In the following, we shall consider a situation in which the applied rf field has its amplitude large enough to induce transitions during the molecular lifetime $(\omega'_1\tau \approx 1)$ and its frequency different enough from ω_0 to affect very little free atoms $(|\omega_0-\omega'| \gg \omega'_1)$.

We shall treat here $\vec{\mathrm{N}}$ as a quantum object. The angular momentum part of the Hamiltonian of a bound molecule is $\mathcal{H}_b(t) = \mathcal{H}_0 + \mathcal{H}'_1(t) + \gamma\vec{\mathrm{S}}\cdot\vec{\mathrm{N}}$; since $\hbar\omega_0 \gg \gamma N$, it is legitimate to replace $\gamma\vec{\mathrm{S}}\cdot\vec{\mathrm{N}}$ by its diagonal part $\gamma\, S_z N_z$:

$$\mathcal{H}_b(t) = (\hbar\omega_0 + \gamma N_z)S_z + \hbar\omega'_1(S_+e^{-i\omega' t} + S_-e^{i\omega' t}). \tag{3.10}$$

(We suppose here $I=0$ for simplicity. It will be easy later to write the final result in the general case $I \neq 0$.) It is convenient for our purpose to work in the interaction representation with respect to the total Hamiltonian of the free atoms

$$\rho(t) = U_f(t)\tilde{\rho}(t)U_f^{\dagger}(t), \tag{3.11}$$

with

$$U_f(t) = e^{-i\omega' S_z t}e^{-i(\omega_0-\omega')S_z t - i\omega'_1 S_x t}. \tag{3.12}$$

(U_f has been written in terms of the evolution operator in the rotating frame.)

The density matrix $\tilde{\rho}(t)$ of atoms of class (b) does not change in time. For atoms of class (a) $\tilde{\rho}(t+\Delta t)$ is obtained from $\tilde{\rho}(t)$ through a relation of the form

$$\tilde{\rho}(t+\Delta t) = \tilde{U}_b(t_0+T, t_0)\tilde{\rho}(t)\tilde{U}_b^{\dagger}(t_0+T, t_0). \tag{3.13}$$

Let us first express $\tilde{U}_b(t_0+T, t_0)$ in terms of the evolution operators $\tilde{U}_b(t)$ satisfying the boundary condition $\tilde{U}_b(t=0)=1$:

$$\tilde{U}_b(t_0+T, t_0) = \tilde{U}_b(t_0+T)\tilde{U}_b^{-1}(t_0). \tag{3.14}$$

Then write $\tilde{U}_b(t)$ as

$$\tilde{U}_b(t) = U_f^{-1}(t)U_b(t), \tag{3.15}$$

where

$$U_b(t) = e^{-i\omega' S_z t}e^{-i[(\omega_0+\hbar^{-1}\gamma N_z-\omega')S_z + \omega'_1 S_x]t} \tag{3.16}$$

is the evolution operator for bound atoms in the laboratory frame. We decided to choose $|\omega' - (\omega_0+\hbar^{-1}\gamma N_z)|$ of the order of ω'_1 but with $|\omega_0 - \omega'| \gg \omega'_1$. We should then keep the term in ω'_1 in $U_b(t)$, but we can set $\omega'_1 = 0$ in $U_f(t)$ at the price of a relative error of the order of $\omega'_1/|\omega_0 - \omega'|$. With this simplification, we compute back $\tilde{U}_b(t_0+T, t_0)$. We end with the following expression:

$$\tilde{U}_b(t_0+T,t_0)=e^{-i(\omega'-\omega_0)t_0S_z}e^{-i(\omega'-\omega_0)S_zT}\times e^{-i\overline{\mathcal{H}}_bT}e^{i(\omega'-\omega_0)t_0S_z}\ , \tag{3.17}$$

with

$$\hbar^{-1}\overline{\mathcal{H}}_b=(\omega_0+\hbar^{-1}\gamma N_z-\omega')S_z+i\omega'_1S_x\ . \tag{3.18}$$

Let us introduce the angle $\phi_0=-(\omega'-\omega_0)t_0$ and use the fact that $e^{i(\omega'-\omega_0)t_0S_z}$ is the unitary operator associated with the rotation of angle ϕ_0 around z to recast $\tilde{U}_b(t_0+T,t_0)$ in the following form:

$$\tilde{U}_b(t_0+T,t_0)=e^{i\gamma_S\hbar^{-1}\vec{S}\cdot\vec{H}_0^eT}e^{i\gamma_S\hbar^{-1}\vec{S}\cdot\vec{H}^eT}\ , \tag{3.19}$$

where the effective dc fields $\vec{H}^e$ and $\vec{H}_0^e$ are given by

$$H_z^e=(\omega_0+\hbar^{-1}\gamma N_z-\omega')\hbar/\gamma_S\ ,$$
$$H_x^e=\omega'_1\cos\phi_0\hbar/\gamma_S\ ,\quad H_y^e=\omega'_1\sin\phi_0\hbar/\gamma_S\ , \tag{3.20}$$

$$H_{oz}^e=(\omega_0-\omega')\hbar/\gamma_S\ ,\quad H_{ox}^e=H_{oy}^e=0\ . \tag{3.21}$$

It is understood that $\tilde{U}_b(t_0+T,t_0)$ operates only on eigenstates of N_z. From the conditions $|\omega_0-\omega'|\gg\omega'_1$, $\omega'_1\tau\sim1$, and $\Delta t\gg\tau$, it follows that $|\phi_0|$ can take, with equal probability, all the values between 0 and $\Delta t|\omega'-\omega_0|\gg1$. It is then legitimate to replace the average over the allowed values of t_0, by an average over ϕ_0 between 0 and 2π. The operator $\tilde{U}_b(t_0+T,t_0)$ is identical to the operator $V(T,\vec{H}_1)$ introduced in Sec. I, provided we make the replacement $\vec{H}_0\to\vec{H}_0^e$ and $\vec{H}\to\vec{H}^e$. In both cases, the averages over the azimuthal angle of $\vec{H}(\vec{H}^e)$ and over T have to be performed in the same way, the other averages being different, of course.

We shall concentrate on the *longitudinal* relaxation rate. The evolution of $\langle\tilde{S}_z\rangle$ in the interaction representation is readily obtained by adapting the results of Sec. I and Ref. 1:

$$\frac{d\langle\tilde{S}_z\rangle}{dt}=-\frac{1}{T'_1(\omega')}\langle\tilde{S}_z\rangle\ , \tag{3.22}$$

with $1/T'_1(\omega')$, for an alkali isotope of nuclear spin I, given by

$$\frac{1}{T'_1(\omega')}=\frac{1}{T_f}\sum_{N,N_z}\mathcal{P}(N,N_z)\times\frac{\omega_1'^2\tau^2}{1+\omega_1'^2\tau^2+[\omega_0+\gamma N_z/\hbar(2I+1)-\omega']^2\tau^2}\ , \tag{3.23}$$

$\mathcal{P}(N,N_z)$ being the probability of finding the molecule in the state N,N_z. (We assume here for simplicity that γ is independent of the vibrational and rotational numbers v, N of the molecule.)

As a function of ω', $1/T'_1(\omega')$ reflects the whole spectrum of the molecular Zeeman transitions ($|\Delta F_z|=1$, $\Delta N_z=0$); it appears as a superposition of Lorentzian lines centered at the discrete values $\omega'=\omega_0+\hbar^{-1}\gamma N_z/(2I+1)$ and having a half-width

$$\Delta\omega=\tau^{-1}(1+\omega_1'^2\tau^2)^{1/2}\ . \tag{3.24}$$

As expected, the effect of the rf field on the relaxation is important only if $\omega'_1\tau\gtrsim1$. If $\Delta\omega\gtrsim\hbar^{-1}\gamma/(2I+1)$, the lines will overlap and $1/T'_1\times(\omega')$ will look like a broad band with a half-width of the order of $\omega^*_1=\hbar^{-1}\gamma N^*/(2I+1)$ (N^{*2} is the average value of $|\vec{N}|^2$). The sum over N and N_z can be replaced by an integral. Writing $\hbar^{-1}\gamma N/(2I+1)=\omega_1$ and $N_z/N=\cos\theta$, we have

$$T_1'^{-1}(\omega')=T_f^{-1}\omega_1'^2\tau^2\int\mathcal{P}(\omega_1)\,d\omega_1\times\int_{-1}^{+1}\frac{\tfrac{1}{2}d(\cos\theta)}{1+\omega_1'^2\tau^2+(\omega_0+\omega_1\cos\theta-\omega')^2\tau^2} \tag{3.25}$$

[$\mathcal{P}(\omega_1)\,d\omega_1$ is the density of probability of ω_1 given in Ref. 1]. One must keep in mind that it is legitimate to use the above formula only if $|\omega_0-\omega'|\gg\omega'_1$. In the vicinity of $|\omega_0-\omega'|=\omega_1^*$, $1/T'_1(\omega^*)$ takes the simplified form

$$T_1'^{-1}(\omega')\simeq\frac{\pi}{4}T_f^{-1}\frac{\omega_1'^2\tau^2}{1+\omega_1'^2\tau^2}\left\langle\frac{\Delta\omega}{\omega_1}\right\rangle_{\text{av}}\ , \tag{3.26}$$

valid for $\omega^*_1\tau\gg1$.

A possible method to detect the effect of a rf field on the relaxation is to look, when the rf field is turned on, for a variation of the stationary value of the electronic polarization $\langle S_z\rangle_\infty$ produced by optical pumping

$$\langle S_z\rangle_\infty=\langle S_z\rangle_{\max}\frac{T_1}{T_p+T_1}\ , \tag{3.27}$$

T_p being the characteristic time of the pumping process. At low-alkali vapor pressure the variation of the stationary polarization $\langle S_z\rangle_\infty$ can be monitored by the transmitted intensity I_d of a detecting beam composed of circularly polarized light, suitably filtered[13]:

$$\delta\langle S_z\rangle_\infty=+\langle S_z\rangle_{\max}\frac{T_pT_1}{(T_p+T_1)^2}\frac{\Delta T_1}{T_1}\propto\delta I_d\ . \tag{3.28}$$

For a given $\Delta T_1/T_1\ll1$, δI_d is maximum if the intensity of the pumping light beam is such that $T_p=T_1$. In the absence of the rf field the main relaxation mechanism when $\hbar\omega_0\gg\gamma N$, is provided by two-body "sudden" collisions. The corresponding time-constant T_1^* is given in Ref. 1. The variation $\Delta T_1/T_1$ due to the action of the rf field on the alkali–rare-gas molecules is given by

$$\Delta T_1/T_1=-T^*_1/T'_1(\omega')\ . \tag{3.29}$$

To obtain the variation of $\langle S_z\rangle_\infty$ resulting from the application of an rf field, we have also to take into account the weak effect of the rf field on *free* alkali atoms. It is most easily obtained from the stationary solution of the Bloch equations in the rotating frame:

$$\delta\langle S_z\rangle_\infty = -\langle S_z\rangle_{\max}\frac{T_p T_1}{(T_p+T_1)^2}\,\frac{T_1}{T_2}\,\frac{\omega_1'^2}{(\omega_0-\omega')^2}\quad . \tag{3.30}$$

Taking $T_2 \sim T_1 = T^*_1$, the ratio of the effect of the rf field on free atoms to that on molecules, when $|\omega_0-\omega'| \sim \omega^*_1$ and $\omega_1'\tau \sim 1$, is

$$\frac{\delta\langle S_z\rangle_\infty\ (\text{free atoms})}{\delta\langle S_z\rangle_\infty\ (\text{molecules})} \sim \frac{\omega_1'^2}{(\omega_0-\omega')^2}\,\frac{T'_1(\omega')}{T^*_1} \sim \frac{\omega_1'}{\omega^*_1}\,\frac{T_f}{T^*_1}\,. \tag{3.31}$$

In a typical case, like the Rb-Kr pair, the above ratio is of the order of 5×10^{-3}, while $T^*_1/T'_1(\omega') = 0.25$ for a Kr pressure of 1 Torr and a rf-field intensity of 1 G ($\omega'_1\tau = 0.3$). These numbers look good enough to allow the study of molecular transitions at a smaller rf-field power and at a lower pressure so that different molecular lines might be resolved.

CONCLUSION

The existence of alkali–rare-gas molecules bound by van der Waals forces leads to very significant effects in the relaxation of ground-state polarized alkali atoms in a rare-gas medium. One of the most striking predictions of our theoretical analysis is perhaps the very peculiar rare-gas pressure dependence of the relaxation parameters (transverse and longitudinal relaxation times; Zeeman-transition line shift). In the pressure range of a few Torr the line shift produced by the collisions leading to molecular association ("sticking" collisions) dominates the other pressure effects for the heaviest rare gases; its sign changes at a given pressure if the dc field is not too large, and it disappears almost completely when the rare-gas pressure reaches 1 atm, the molecules then becoming too unstable to play any role. The anomalous pressure dependence of the hyperfine transition linewidth discovered by Bender and Cohen is quantitatively explained by the "sticking" collisions mechanism. The action of a rf field on the alkali atoms has been subjected to a theoretical investigation. The most promising situation occurs when the frequency of the dc field falls among the transition frequencies of the bound atom. The predicted effects on the relaxation processes appear strong enough to allow a study of the molecular fine structure due to the molecular spin-orbit coupling $\gamma\vec{S}\times\vec{N}$ interaction which is held responsible for most of the relaxation effects studied here. An experimental program of systematic verification of the predictions of this paper has been started at the Ecole Normale Superieure and will certainly contribute to our knowledge of van der Waals molecules not easily accessible to experimental study by more conventional methods.

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*Associé au Centre National de la Recherche Scientifique, Paris, France.

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