PHYSICAL REVIEW VOLUME 181, NUMBER 1 5 MAY 1969

Evidence for Rb-Rare-Gas Molecules from the Relaxation of Polarized Rb Atoms in a Rare Gas. Theory

C. C. Bouchiat

*Laboratoire de Physique Théorique et Hautes Energies, Faculté des Sciences d'Orsay, Orsay, France**

and

M. A. Bouchiat and L. C. L. Pottier

*Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure, Faculté des Sciences de Paris, Paris, France**

(Received 21 October 1968)

Relaxation experiments performed on optically polarized Rb atoms in a rare gas have been previously reported; their detailed interpretation is given below. It is 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. Two processes of molecule formation are analyzed: binary resonant collisions leading to metastable states and three-body collisions producing actual bound states. A relaxation model valid for any disorientation probability per single Rb-Kr interaction is developed. Aside from clear evidence for the existence of alkali-rare-gas molecules, the success of the theoretical interpretation of the relaxation experiments yields the equilibrium constant $\mathcal{K} = 1.7 \times 10^{-22}\,\mathrm{cm}^3$/molecule for the reaction Rb + Kr $\rightleftharpoons$ Rb-Kr at 300°K, the average lifetime of a Rb-Kr molecule in the gas phase, $\tau = 0.65 \times 10^{-7}$ sec, at a krypton pressure of one Torr, and the average spin-orbit coupling constant in a Rb-Kr molecule, $\bar{\gamma} h^{-1} = 0.63$ MHz. It is also shown that the spin-orbit potential is predominantly short-range.

I. INTRODUCTION

Relaxation of alkali atoms in a diamagnetic buffer gas usually involves two mechanisms: it is induced (a) by wall collisions after diffusion through the gas, (b) by collisions against the gas molecules. The problem has been reinvestigated recently under different experimental conditions so that mechanism (b) becomes the dominant one. Experiments were also performed in a wider pressure range.[1] The results obtained for the Rb-Kr pair look at first glance quite puzzling:

(i) the relaxation rates of $\langle S_z \rangle$ depend strongly on the magnetic field, while no field dependence is expected up to several thousand gauss for collisions lasting for a time of the order of 10^{-12} sec, a typical value for binary-collision duration in the gas phase.

(ii) In low fields the same relaxation rates are *not* proportional to the gas pressure P. This also is unexpected, because any relaxation mechanism involving binary Rb-Kr collisions should lead to a relaxation rate proportional to the collision rate, i.e., to P. On the other hand, above 200 G, relaxation rates become proportional to P.

The purpose of the present paper is to give a theoretical interpretation of these relaxation experiments. Owing to the peculiar field and pressure dependence of the relaxation rates, the experimental data are rich enough to allow a detailed description of the disorienting mechanism. The paper is organized in the following way: First (Sec. II), the general form of the interaction between a rare gas having zero nuclear spin and an alkali atom is deduced from simple invariance considerations. It is argued that the relaxation of Rb atoms by collisions against rare gas atoms without nuclear spin is likely to be governed by the spin-orbit interaction. Then, in Sec. III, different types of Rb-Kr collisions are analyzed; emphasis is put on parameters playing an essential role in the relaxation mechanism: the collision rate and the duration of the disorienting interaction. A sharp distinction appears between the binary collisions which last only a few 10^{-12} sec (hereafter called "sudden" two-body collisions) and the three-body collisions which lead to the formation of Rb-Kr molecules loosely bound by van der Waals forces and likely to be destroyed at the next collison against a Kr atom. From the energy spectrum of the Rb-Kr molecule the equilibrium constant of the Rb + Kr $\rightleftharpoons$ Rb-Kr reaction is computed. A crude estimate of excitation and break-up cross sections is given for collisions between a Rb-Kr molecule and a Kr atom. We study also the process of formation of molecular metastable states by two-body resonant collisions.

Next (Sec. IV), we turn to the relaxation problem itself. For "sudden" two-body collisions, perturbation relaxation theory can be used because these collisions are weak; the motional narrowing condition is satisfied. However, this is no longer always true for collisions leading to the formation of Rb-Kr molecules; at a low Kr gas pressure a molecule lives long enough to allow $\vec{S}$ to perform a complete precession around the total molecular angular momentum $\vec{N}+\vec{S}$ so that the spin-flip probability is of the order of unity. Consequently we have developed (in Sec. V) a model of relaxation valid for any value of the spin-flip probability per single Rb-Kr interaction. We obtain the explicit dependence of the relaxation rate versus the gas pressure, the temperature and the dc field in terms of averaged physical parameters. In Sec. VI, we show that the relaxation theory proposed in this paper gives a satisfactory interpretation of experimental results. The field-dependent part of the relaxation is associated with collisions leading to formation of molecules. The predicted theoretical pressure and field variations are well reproduced experimentally. "Sudden" two-body collisions account for the relaxation rates measured at field values larger than 200 G. From a fit of theoretical curves with experimental data, we obtain values for the physical parameters of the theory (the equilibrium constant, the averaged collision lifetime and the averaged spin-orbit coupling constant for a Rb-Kr molecule), which agree with theoretical estimates. Finally a comparison of the relaxation rates measured at 0 and 200 G yields some information about the range of the spin-orbit potential.

II. INTERACTIONS BETWEEN A ZERO-NUCLEAR-SPIN RARE GAS AND AN ALKALI ATOM

We shall describe the interaction between a rare-gas atom of spin 0 and an alkali atom of nuclear spin $\vec{I}$ and electronic spin $\vec{S}$, by a potential $U(\vec{r}, \vec{p}, \vec{I}, \vec{S})$, where $\vec{r}$ and $\vec{p}$ are the relative coordinate and momentum of the two atoms. We shall first restrict our discussion to the case $S = I = \frac{1}{2}$. We shall deal later with the case in which I takes an arbitrary value. Keeping only terms linear in the momentum,[2] the most general potential compatible with invariance under space rotation, space reflection and time reversal can be shown to be of the form

$$\begin{aligned} U = U(r) &+ [a+\alpha(r)]\vec{S}\cdot\vec{I} \\ &+ \beta(r)[(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})/r^2 - \tfrac{1}{3}\vec{S}\cdot\vec{I}] \\ &+ \gamma(r)\vec{S}\cdot\vec{N} + \delta(r)\vec{I}\cdot\vec{N} \ , \end{aligned} \qquad (1)$$

where $\hbar\vec{N} = \vec{r}\times\vec{p}$ is the relative orbital angular momentum of the two atoms.

The dominant term is obviously the purely central term $U(r)$ which describes the electrostatic and exchange forces between the constituents of the two atoms. Atom-atom scattering experiments, at low energy,[3] have been analyzed in terms of a $U(r)$ of the 12-6 Lennard-Jones type:

$$U(r) = \epsilon[(r_m/r)^{12} - 2(r_m/r)^{6}] \ . \qquad (2)$$

For the Rb-Kr pair, experimental results can be fitted with $\epsilon = 10^{-2}$ eV and $r_m = 4.53$ Å (r_m is the value of r for which $U(r)$ is minimum and equal to $-\epsilon$).

The other terms in U, which play a negligible role in the scattering process, govern the relaxation of polarized Rb atoms. As a consequence of time-reversal invariance, no electrostatic interaction (including exchange) can remove completely the degeneracy of a system of 2 atoms for which the total electronic angular momentum is half-integral (Kramers theorem). So in the present case spin-dependent interactions have necessarily a magnetic origin and are consequently quite small.

We discuss now each term of U separately. The hyperfine interaction $a\vec{S}\cdot\vec{I}$ for free alkali atoms is modified by the quantity $\alpha(r)$ which describes the effect of the distortion of the ^1s electronic wave function during a collision. Since we shall deal only with experiments concerning longitudinal relaxation in a relatively low magnetic field, our prepared system of polarized Rb atoms shall be described by a density matrix diagonal with respect to $\vec{F}^2 = (\vec{I}+\vec{S})^2$ and $F_z = I_z + S_z$, so that the interaction $\alpha(r)\vec{S}\cdot\vec{I}$ will not participate in the relaxation process.

It is likely that the nuclear spin-orbit interaction $\delta(r)\vec{I}\cdot\vec{N}$ is smaller than the electronic spin-orbit interaction $\gamma(r)\vec{S}\cdot\vec{N}$ by a factor of the order of the ratio of the electron to the nucleon mass, but there is no *a priori* argument to tell which one of the two: spin-orbit interaction $\gamma(r)\vec{S}\cdot\vec{N}$ or anisotropic hyperfine interaction

$$\beta(r)[(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})/r^2 - \tfrac{1}{3}\vec{S}\cdot\vec{I}] \ ,$$

is the dominant one. In the simple case of the H_2^+ molecule, calculations have been made; both come out with the same order of magnitude.[4] For the case of the Rb-Kr pair, only the spin-orbit coupling interaction has been estimated by Herman.[5] To prove that the spin-orbit interaction is likely to be the dominant one, it is necessary to refer to the results of a phenomenological analysis of relaxation measurements performed on the two isotopes of Rb $[I(^{87}\text{Rb}) = \frac{3}{2}$, and $I(^{85}\text{Rb}) = \frac{5}{2}]$. In the case where the motional narrowing condition is satisfied, theory predicts that the mean value of $\langle\vec{S}\cdot\vec{I}\rangle$ relaxes with only one time constant T_H while the time evolution of the electronic polarization $\langle S_z\rangle$ is governed by two time constants T_e and T_n. It can be shown that for a Zeeman splitting associated with a magnetic field of about 200 G, the ratios between the time constants T_H, T_e, T_n relative to the two isotopes can be predicted both for the spin-orbit interaction[6] and for the anisotropic hyperfine interaction.[7] Table I summarizes the theoretical predictions one obtains when the correlation time is assumed to be shorter

TABLE I. Theoretical and experimental relaxation rates. The numbers presented in this table are the ratios between the relaxation rates of different observables relative to an ensemble of ^{87}Rb or ^{85}Rb atoms. T_H^{-1}, T_n^{-1}, and T_e^{-1} refer respectively to the relaxation rates of $\langle \vec{S}\cdot\vec{I}\rangle$, $\langle I_z\rangle$, and $\langle Q_e\rangle = \langle S_z\rangle - \{2/[(2I+1)^2-2]\}\langle I_z\rangle$. The values predicted by theory when it is assumed that the disorienting interaction is either the spin-orbit ($\vec{S}\cdot\vec{N}$) or the anisotropic hyperfine interaction are compared to the experimental values measured at 200 G for the relaxation of Rb induced by collisions with Kr.

		Theoretical values		Measured values[1] with experimental accuracy for Rb-Kr
		$\vec{S}\cdot\vec{N}$ interaction	anisotropic hf interaction	
^{87}Rb	T_e/T_H	1	1.09	1 ± 0.15
	T_n/T_H	8	1.6	8.5 ± 0.6
^{85}Rb	T_e/T_H	1	1.035	1 ± 0.15
	T_n/T_H	18	3.79	18.1 ± 1.8
	T_n^{85}/T_n^{87}	2.25	0.89	2.1 ± 0.16

than the inverse of the hyperfine frequency $\hbar\Delta W^{-1}$.[8] Experimental results shown also in Table I favor unambiguously the spin-orbit interaction as the dominant one.

For an alkali nuclear spin I larger than $\frac{1}{2}$, invariance principles allow types of interactions other than those just discussed. They will contain higher-order tensors built from the nuclear spin operator $\vec{I}$. During the collision an electric field gradient will appear along the line joining the 2 atoms; it will couple with the quadrupole moment of the nucleus, giving rise to an interaction of the form

$$g(r)[(\vec{I}\cdot\vec{r})(\vec{I}\cdot\vec{r})/r^2 - \tfrac{1}{3}\delta_{ij}\vec{I}^2] .$$

A crude estimate of its order of magnitude can be obtained in the following way. The same interaction plays a predominant role in the nuclear relaxation of a rare gas (with $I\neq\frac{1}{2}$) induced by collisions between identical atoms. The case of ^{131}Xe has been investigated in detail.[9] If one assumes an order of magnitude not too different for the Rb-Kr pair, it will certainly play a negligible role in the relaxation of Rb atoms. Furthermore it can also be eliminated owing to arguments similar to those used above for the anisotropic hyperfine interaction.

In conclusion we shall assume in the rest of the present paper that the relaxation of Rb atoms by collisions against rare-gas atoms without nuclear spin is governed by the spin-orbit interaction $\gamma(r)\vec{S}\cdot\vec{N}$.

III. GENERAL PROPERTIES OF THE Rb-Kr SYSTEM

A. Introduction

The experimental results recalled in the introduction suggest that the stochastic spin-dependent interaction between a rare gas and an alkali atom has an unexpectedly long correlation time. As a first explanation, one might think that the disorienting interactions relative to two successive collisions might be correlated. This would imply the presence, in the correlation function, of a characteristic time of the order of the time of flight. However, a detailed analysis shows that even if such a supposed correlation should exist it could not account for the *amplitude* of the observed variation of relaxation time constants with the Zeeman splitting.

As we shall show in the rest of this paper, the correct explanation for this long correlation time seems to go along the following lines: A Rb and a Kr atom have a certain probability to stick together (mainly after a three-body collision), giving rise to a Rb-Kr molecular state likely to be destroyed at the next collision. The disorienting interaction will then last for the lifetime of this molecular state, i.e., roughly the time of flight, 10^{-7} to 10^{-9} sec, for a Kr pressure varying between 0.1 and 10 Torr.

In this section, after a short review of the two-body problem for a Rb-Kr pair, we shall describe the energy spectrum of Rb-Kr bound and resonant states. Using statistical-mechanics considerations, we shall evaluate the fraction of Rb atoms engaged in a Rb-Kr molecular state at a given time. A very crude estimate of excitation and break-up cross-sections for a Rb-Kr molecule collision with a Kr atom will be given. Finally, the lifetime and production cross sections of resonant states in two-body collisions will be discussed.

B. The Two-Body Problem

The relative motion of the Rb-Kr pair is reduced to the motion of the relative particle of mass

$$\mu = M_{\mathrm{KR}} M_{\mathrm{Rb}}/(M_{\mathrm{Kr}} + M_{\mathrm{Rb}})$$

and energy $E = p^2/2\mu$, in the effective potential

$$U_N(r) = U(r) + N(N+1)\hbar^2/2\mu r^2 \quad , \tag{3}$$

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

Typical shapes of $U_N(r)$ are given for different values of N (Fig. 1). For $0 < N < N_c$, $U_N(r)$ has the shape of a potential well protected by a centrifugal barrier. The phase space allowed for the relative particles can be decomposed into three domains corresponding to the regions I, II, and III of the (E, r) diagram of Fig. 2. The states in region I are ordinary bound states which can be formed and destroyed only in three-body collisions. Region II corresponds to metastable states. They can decay via the tunnel effect, but apart from a few states in the vicinity of the top of the barrier, their natural lifetimes are much longer than the time of flight of the pair, so that they can be treated on the same footing as true bound states. The states in phase-space region III are the normal diffusion states. When $0 < E < E_{\max}(N)$, the relative particle has a finite probability of passing to region II because of the tunnel effect, but this probability is negligible unless E is equal to the energy of a metastable state near the top of the barrier. For these few cases, we are dealing with a resonant diffusion with a collision time given by the lifetime of the corresponding metastable state. In all other cases, the incident particle is reflected and the disorienting interaction will act for a period of the order of the range of the spin-dependent potential divided by the velocity of the relative particle; this is what we call a "sudden" two-body collision.

It thus appears that we have to deal with two very different kinds of collisions: "sudden" collisions having a large rate, but a short duration, and "sticking" collisions (i.e., three-body collisions or two-body resonant collisions, yielding the formation of a molecule), which have a smaller rate, but which lead to quite a long Rb-Kr interaction. Before investigating the relaxation process induced by collisions of each type, we analyze below a few characteristics of the "sticking" collisions.

C. Energy Spectrum of Bound and Metastable States

The energy of the bound states can be obtained with good accuracy in the semiclassical approximation, using the Bohr-Sommerfeld quantization rule

$$h(v+\tfrac{1}{2}) = 2\int_{r_1}^{r_2} p(r)\,dr \quad , \tag{4}$$

with

$$p(r) = \{2\mu[E(v,N) - U(r) - \hbar^2(N+\tfrac{1}{2})^2/2\mu r^2]\}^{1/2} \quad , \tag{5}$$

and v an arbitrary zero or positive integer; r_1 and r_2 stand for the classical turning points. Following the usual prescription, we have replaced $N(N+1)$ by $(N+\frac{1}{2})^2$ in the expression of the centrifugal potential. For different values of v

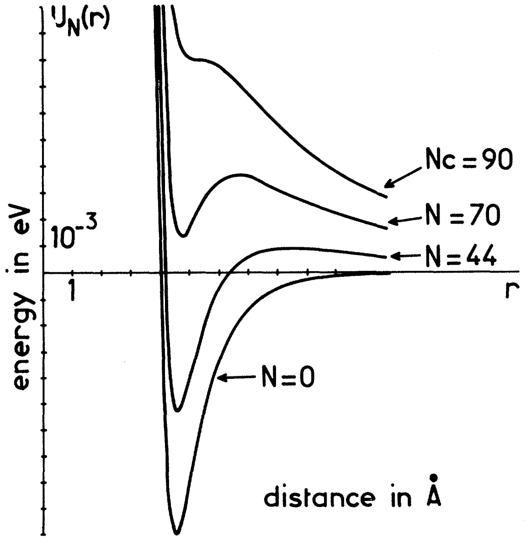

FIG. 1. Typical shapes of the effective potential $U_N(r)$ for various values of N, computed for a Lennard-Jones 12-6 potential. ($r_m = 4.53$ Å; $\epsilon = 10^{-2}$ eV).

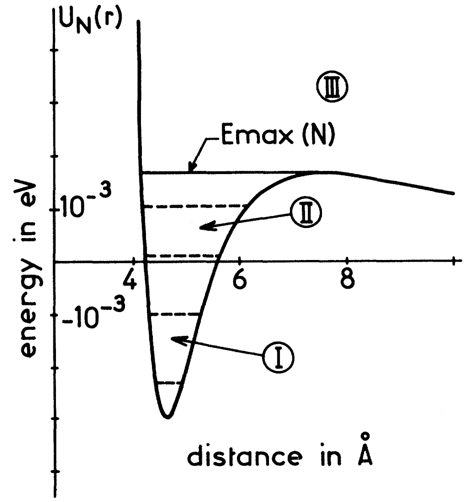

FIG. 2. Phase space allowed to the relative particle describing the relative motion of a Rb-Kr pair characterized by the relative angular momentum $N\hbar$: region I corresponds to actual bound states, region II to metastable states, and region III to normal diffusion states.

the energies $E(v,N)$ plotted as a function of $(N+\frac{1}{2})^2$ in Fig. 3 appear as straight lines.[10] The energy $E(v,N)$ is given as a sum of two terms:

$$E(v,N)=E_v+\hbar^2(N+\tfrac{1}{2})^2/2I(v) \ , \tag{6}$$

with $0 \leqslant N \leqslant N_{\max}(v)$.

The first term independent of N is interpreted as a vibrational energy. The second term is a rotational energy, the moment of inertia $I(v)$ being a slowly varying function of the vibrational number v. The rotational band is cut off at an integral value $N_{\max}(v)$, which is the largest integral value of N such that inequality

$$E(v,N) \leqslant E_{\max}(v,N)$$

holds.

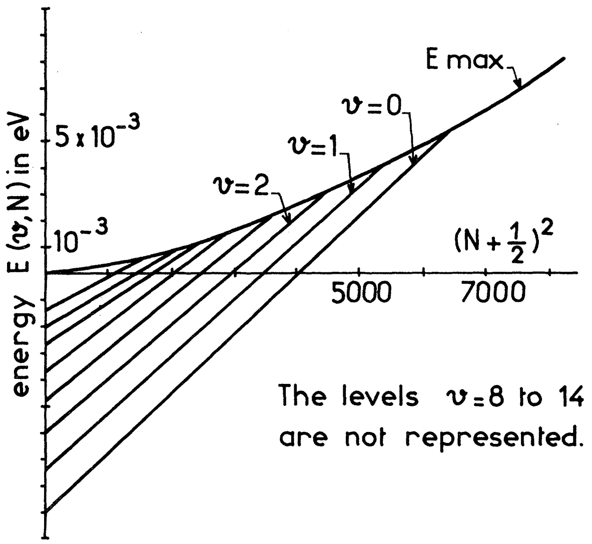

FIG. 3. Energies of the different rotational-vibrational molecular states of the Rb-Kr pair computed for a Lennard-Jones 12-6 potential ($r_m=4.53$ Å; $\epsilon=10^{-2}$ eV), by using the W.K.B. approximation.[10]

D. Equilibrium Populations of the Rb-Kr Molecular States

Let us consider a Rb-Kr pair. The total number of pairs is $N_{\mathrm{Kr}}N_{\mathrm{Rb}}$ where N_{Kr} and N_{Rb} are the total number of Kr and Rb atoms in the volume $\mathcal{V}$. We are concerned with the case for which $N_{\mathrm{Rb}} \ll N_{\mathrm{Kr}}$. The probability of finding a pair Rb-Kr in a bound state (v,N) having energy $E(v,N)$ is given, assuming thermal equilibrium, by

$$\mathcal{P}(v,N)=(2N+1)e^{-\beta E(v,N)}/\sum_j g_j e^{-\beta E_j} \ . \tag{7}$$

The sum $\sum_j$ runs over all states E_j of the discrete and continuous spectrum of the Rb-Kr pair, g_j being the multiplicity of the level E_j. The contribution of the discrete spectrum reads

$$\sum_v \sum_{N\leqslant N_{\max}(v)} (2N+1)e^{-\beta E(v,N)} \ ,$$

and the one of the continuous spectrum is

$$\mathcal{V}h^{-3}\int d^3p\, e^{-\beta p^2/2\mu}=\mathcal{V}\lambda_T^{-3} \ ,$$

with $\lambda_T=\hbar(2\pi\beta/\mu)^{1/2}$. (8)

(In the unbound pair associated with region III, the particles are considered as free particles. This is legitimate since we are working with a gas at low pressure). For the Rb-Kr pair at 300°K, $\lambda_T=1.58\times10^{-9}$ cm. The volume $\mathcal{V}$ is of the order of a few cubic centimeters; so, the number of states in the continuum is much larger than the total number of bound and metastable states, which is around 3×10^4, and we can write $\mathcal{P}(v,N)$ as

$$\mathcal{P}(v,N)=\lambda_T^{3}\mathcal{V}^{-1}(2N+1)e^{-\beta E(v,N)} \ . \tag{9}$$

The total number of Rb-Kr molecules in a (v,N) state is given by

$$n(v,N)=N_{\mathrm{Kr}}N_{\mathrm{Rb}}\,\mathcal{P}(v,N) \ ,$$

and the fraction of Rb atoms in a (v,N) molecular state by

$$n(v,N)/N_{\mathrm{Rb}}=N_{\mathrm{Kr}}\,\mathcal{P}(v,N) \ . \tag{10}$$

Apart from the Boltzmann factor, which is not too different from unity at 300°K, this ratio does not depend on v; it is proportional to the multiplicity $2N+1$ of the state. For a mixture of Rb and Kr *at one atmosphere of* Kr, the total fraction of Rb atoms engaged in all molecular states is obtained, after computation[11] of $\sum_{v,N}\mathcal{P}(v,N)=3.70\times10^4$, as

$$\frac{n_{\mathrm{Rb\text{-}Kr}}}{N_{\mathrm{Rb}}}=\frac{\sum_v \sum_{N\leqslant N_{\max}(v)} n(v,N)}{N_{\mathrm{Rb}}}=3.56\times10^{-3} \ . \tag{11}$$

Equation (11) is just the law of mass action written for the equilibrium condition Rb + Kr ⇄ Rb-Kr. We have deduced[11] the equilibrium constant

$$\mathcal{K}=n_{\mathrm{Rb\text{-}Kr}}\,\mathcal{V}/N_{\mathrm{Rb}}N_{\mathrm{Kr}}$$

from considerations of pure statistical theory:

$$\mathcal{K}=\mathcal{V}\sum_v \sum_{N\leqslant N_{\max}(v)} \mathcal{P}(v,N)$$

$$=1.46\times10^{-22}\text{cm}^3/\text{molecule}, \tag{12}$$

at 300°K.

Before closing this section we would like to give a simple relation which will be of some use later. Let $\tau(v,N)$ be the lifetime of a molecular state (v,N) of given energy and $T_f^{\,-1}(v,N)$ the probability per unit time for the capture of a Rb atom into that same Rb-Kr molecular state. Writing that, at equilibrium, the number of molecular states produced is equal to the number of states destroyed per unit time, we obtain the relation

$$n(v,N)/\tau(v,N)=N_{\text{Rb}}/T_f(v,N)\,, \tag{13}$$

or

$$\tau(v,N)/T_f(v,N)=N_{\text{Kr}}\,\mathcal{P}(v,N)\,. \tag{14}$$

Later we shall assume that all molecular states involved have the same lifetime τ. The formation rate of a Rb-Kr molecule

$$T_f^{\,-1}=\sum_{v,N}T_f(v,N)^{-1}$$

then satisfies the relation

$$\tau/T_f=n_{\text{Rb-Kr}}/N_{\text{Rb}}=N_{\text{Kr}}\,\mathcal{V}^{-1}\mathcal{K}\,. \tag{15}$$

E. Break-Up and Excitation Cross Sections of Rb-Kr Molecules

We present now a crude evaluation of the inelastic scattering cross sections of a Rb-Kr molecule by a Kr atom. A full treatment of the three-body problem involved is obviously out of the question, and we will have to rely on approximations which are not always fully justified. Our discussion will be a classical one; quantum effects are certainly present, but they do not affect the gross structure of the scattering process. We shall also assume that Rb-Kr and Kr-Kr interactions are identical.

(1) *The break-up cross section* will be discussed first. Let us introduce the two following average break-up energies: $\overline{\Delta E_r}$ and $\overline{\Delta E_v}$, defined as follows:

$$\overline{\Delta E_v}=\sum_{v,N}\mathcal{P}(v,N)[E(v_{\max}(N),N)-E(v,N)]\Big/\sum_{v,N}\mathcal{P}(v,N)\,,$$

$$\overline{\Delta E_r}=\sum_{v,N}\mathcal{P}(v,N)[E(v,N_{\max}(v))-E(v,N)]\Big/\sum_{v,N}\mathcal{P}(v,N)\,,$$

where $v_{\max}(N)$ $[N_{\max}(v)]$ is the highest vibrational [rotational] number for a given value of N $[v]$; $\overline{\Delta E_r}$ $[\overline{\Delta E_v}]$ corresponds to a transition where the energy is transferred to the molecule only in the form of rotational [vibrational] energy. Using the results of Sec. III C, one finds numerical values for $\overline{\Delta E_r}$ and $\overline{\Delta E_v}$:

$$\overline{\Delta E_r}=0.45\epsilon=4.5\times10^{-3}\text{ eV},\quad \overline{\Delta E_v}=0.26\epsilon=2.6\times10^{-3}\text{ eV}\,. \tag{16}$$

These numbers have to be compared with the average kinetic energy of the incident Kr atom in the rest frame of the molecule

$$E_i=\tfrac{9}{4}\beta^{-1}=5.6\epsilon=5.6\times10^{-2}\text{ eV}\,. \tag{17}$$

To have a rough idea of the break-up cross section, we use the classical analog of the impulse approximation: the incident Kr atom is assumed to interact only with one of the two atoms of a Rb-Kr molecule, the other atom acting as a spectator. Such an assumption is justified only when the classical rotational and vibrational periods of the molecule are much longer than the collision time; this is probably realized for collisions having a small impact parameter. The binding energy and the kinetic energy of the atoms of the Rb-Kr molecule are neglected with respect to the kinetic energy of the incident atom. Let χ be the scattering angle in the center-of-mass frame of the two interacting atoms, the kinetic energy given to the target atom (assumed to be initially at rest) being $E_i\sin^2\chi/2$. If the mass of Kr and Rb atoms are taken to be equal, half of this energy will be transferred as vibrational and rotational energy of the molecule, the rest of it being found as kinetic energy of the center of mass.

The geometry of the collision is specified in Fig. 4. We have denoted by A the center of mass of the atom of the molecule interacting with the incoming Kr atom. B is the center of mass of the other atom and O the c.m. of the molecule. $\vec{p}_A$ is the recoil momentum of A, η and ξ define the direction of the molecular axis with respect to the direction of the Kr atom incoming with momentum $\vec{p}_i$. The quantity ψ denotes the angle of $\vec{p}_A$ with the molecular axis.

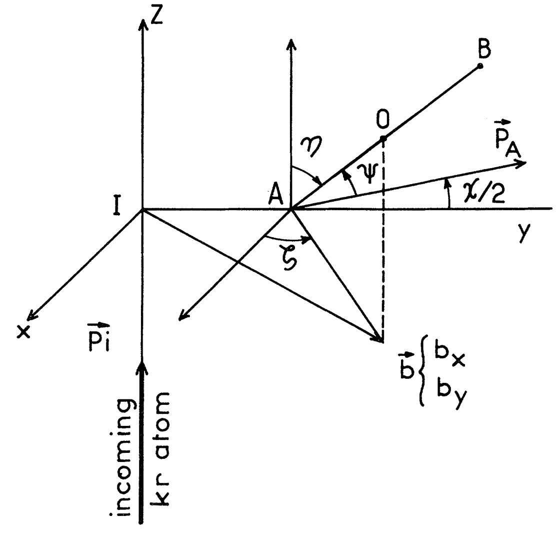

FIG. 4. Coordinate system used to specify a collision between a Rb-Kr molecule and a Kr atom.

The energies transferred to the molecule as vibrational and rotational energies are, respectively,

$$\delta E_v = \tfrac{1}{2} \cos^2\psi \sin^2(\chi/2)E_i\,, \quad \delta E_r = \tfrac{1}{2} \sin^2\psi \sin^2(\chi/2)E_i\,. \tag{18}$$

The total energy $\delta E_v + \delta E_r = \frac{1}{2}(\sin^2\chi/2)E_i$, necessary to break-up a molecule, depends on the angle ψ. The average break-up energy $\Delta = \langle \delta E_v + \delta E_r \rangle_{\rm av}$, averaged over ψ and the initial molecular state, can be readily calculated in terms of $\overline{\Delta E_v}$ and $\overline{\Delta E_r}$, if the curvature of the curve $E_{\rm max}(N)$ of the energy diagram (Fig. 3) is neglected. One finds $\Delta \simeq 0.37\epsilon = 3.7 \times 10^{-3}$ eV.

Let us for a moment forget about atom B. The differential two-body cross section $d\sigma/d(\sin^2\chi/2)$ for the scattering angles involved here, is nearly constant, so that the average break-up cross section neglecting atom B is simply πb_0^2, where the impact parameter $b_0 = 0.89 r_m$ corresponds[12] to the scattering angle χ_0 given by

$$\tfrac{1}{2} E_i \sin^2\chi_0/2 = \Delta\,.$$

If the two atoms A and B were very far apart the break-up cross section would be simply $2\pi b_0^2$. But the two spheres of radius b_0 centered at A and B overlap, and instead of the factor 2, a simple geometrical factor $s(b_0, \eta)$ depending on η has to be inserted. One can check that the break-up energy depends only weakly on η so that $s(b_0,\eta)$ can be readily averaged. The average break-up cross section in our simple impulse approximation is then given by

$$\bar{\sigma}_b = \pi b_0^2 \int s(b_0, \eta)\, d(\cos\eta) \Big/ \int d(\cos\eta) = 1.53 \pi b_0^2 = 1.2 \pi r_m^2\,. \tag{19}$$

The above estimate is obviously very crude and multiple-scattering corrections are certainly not negligible. Nevertheless we believe that we have obtained the right order of magnitude.

(2) We shall now discuss the scattering process involving an *excitation of the molecule* with a certain transfer $\overrightarrow{\Delta \mathrm{N}}$ of orbital angular momentum. Let us call $\overline{N}$ the average angular momentum of our ensemble of Rb-Kr molecules. We shall by convention call scattering collisions such that $|\Delta N|/\overline{N} < 0.1$ purely elastic, since the spin-orbit interaction $\gamma \vec{\mathrm{S}} \cdot \vec{\mathrm{N}}$ is practically not affected by the collision (we neglect the effect on γ of a change of vibrational number). We shall discuss only the small-angle scattering for which $\overrightarrow{\Delta \mathrm{N}}$ is certainly small. To evaluate $\overrightarrow{\Delta \mathrm{N}}$ we shall approximate the trajectory of the incoming atom by a straight line and write $\hbar \overrightarrow{\Delta \mathrm{N}} = \int_{-\infty}^{+\infty} (\overrightarrow{\mathrm{OA}} \times \vec{\mathrm{F}}_A + \overrightarrow{\mathrm{OB}} \times \vec{\mathrm{F}}_B)\, dt$, where O is the center of mass of the molecule and $\vec{\mathrm{F}}_A$ and $\vec{\mathrm{F}}_B$ the forces acting on atoms A and B. Since we are interested in the large impact parameter collisions, we shall take only the attractive part of the Lennard-Jones potential. When $\eta = \pi/2$, the quantity $\overrightarrow{\Delta \mathrm{N}}$ is along the trajectory of the incident particle and given by

$$\Delta N = c b_x r_m^{\,6} \{ [(\tfrac{1}{2} r_m - b_y)^2 + b_x^{\,2}]^{-7/2} - [(\tfrac{1}{2} r_m + b_y)^2 + b_x^{\,2}]^{-7/2} \}\,, \tag{20}$$

with $c = \frac{5}{4}\pi\sqrt{3}\, \epsilon r_m / \hbar \overline{V}_r = 121\,,$ (21)

b_x and b_y being the components of the impact parameter $\vec{b}$ relative to the center of mass of the molecule (see Fig. 4), and $\overline{V}_r$ the relative velocity of two Rb and Kr free atoms averaged over the thermal distribution.

The relation $|\Delta N| = 0.1\overline{N}$ defines a certain closed curve $\mathcal{C}$ in the xy plane perpendicular to the incident momentum. For b outside this curve the transferred angular momentum is such that $|\Delta N| \leq 0.1\overline{N}$. The area enclosed in the curve gives an upper limit of the cross section for scattering with $\eta = \pi/2$ and $|\Delta N| > 0.1\overline{N}$. One finds

$$\sigma(\eta = \pi/2, |\Delta N| > 0.1\overline{N}) \leq 3.4\pi r_m{}^2 . \tag{22}$$

Since $\Delta N = 0$ for $\eta = 0, \pi$, it is necessary to perform an average over η:

$$\sigma(|\Delta N| > 0.1\overline{N}) = \int \sigma(\eta, |\Delta N| > 0.1\overline{N})\, d\cos\eta \Big/ \int d\cos\eta \leq 3.3\pi r_m{}^2 . \tag{23}$$

One can verify that practically all the collisions leading to a break-up of the molecule have their impact parameters lying inside $\mathcal{C}$. Then, an upper bound of the excitation cross section of the molecule is obtained by substracting from the above bound the break-up cross section

$$\sigma_e(|\Delta N| > 0.1\overline{N}) \leq 3.3\pi r_m{}^2 - \overline{\sigma}_b \sim 2\pi r_m{}^2 . \tag{24}$$

In conclusion, it seems safe to say that the excitation cross section with $|\Delta N| > 0.1\overline{N}$ is at most of the same order of magnitude ($\pi r_m{}^2$) as the break-up cross section.

F. Natural Lifetimes and Two-Body Excitation Cross Sections of Metastable States

The natural lifetime of metastable states can be obtained by semi-classical consideration.[13] If we call τ_0 the classical period of oscillation of the relative particle in the potential well,

$$\tau_0 = 2\int_{r_1}^{r_2} \frac{\mu\, dr}{p(r)} = 2\int_{r_1}^{r_2} \left(\frac{2}{\mu}[E - U_N(r)]\right)^{-1/2} dr , \tag{25}$$

the decay probability per unit time τ^{-1} is obtained by multiplying $\tau_0{}^{-1}$ by the transmission coefficient D:

$$\tau^{-1} = D\tau_0{}^{-1} . \tag{26}$$

We shall be interested here in metastable states near the top of the centrifugal barrier ($r = r_{\text{max}}$). The effective potential is approximated by a parabola

$$U_N(r) = E_{\text{max}}(N) - \tfrac{1}{2}\mu\omega_N{}^2(r - r_{\text{max}})^2 . \tag{27}$$

The transmission coefficient is given rigorously by

$$D^{-1} = 1 + \exp\{2\pi[E_{\text{max}} - E(v,N)]/\hbar\omega_N\} .$$

For a small value of D one can use the approximate formula

$$D(v,N) \approx \exp\{-2\pi[E_{\text{max}} - E(v,N)]/\hbar\omega_N\} . \tag{28}$$

The total lifetime of a metastable state is given by

$$1/\tau^t(v,N) = 1/\tau^c(v,N) + D(v,N)/\tau_0 . \tag{29}$$

The lifetime due to collisions $\tau^c(v,N)$ is of the same order of magnitude as the time of flight defined conventionally as

$$\tau_f{}^{-1} = N_{\text{Kr}} \mathcal{V}^{-1} \pi r_m{}^2 \overline{V}_r , \tag{30}$$

and equal to 1.25×10^{-7} sec at a Krypton pressure of 1 Torr.[14] For the range of Kr pressures involved in the experiments (0,1 Torr to 20 Torr), τ_f varies between 1.25×10^{-6} sec and 0.62×10^{-8} sec. The metastable states, the natural lifetime of which is much larger than 10^{-6} sec, will behave like true bound states, but a special treatment is needed for metastable states of shorter natural lifetime ($\leq \tau_f$).

To get an accurate estimate of the natural lifetime is a very difficult if not impossible task. The reason is the exponential dependence of the transmission coefficient upon the energy of the metastable state. For a given vibrational number v, we have seen that the energy $E(v,N)$ is given by Eq. (6) for $N \leq N_{\text{max}}$. Let us call N_v the solution of the equation $E(v,N) - E_{\text{max}}(N) = 0$, where $E_{\text{max}}(N)$ is the top of the centrifugal barrier. The integer N_{max} can be written in terms of N_v as

$$N_v = N_{\text{max}}(v) + \eta_v , \tag{31}$$

with $0 < \eta_v < 1$ (see Fig. 5). The transmission coefficient for the metastable states lying near the top of the barrier is given in terms of η_v by

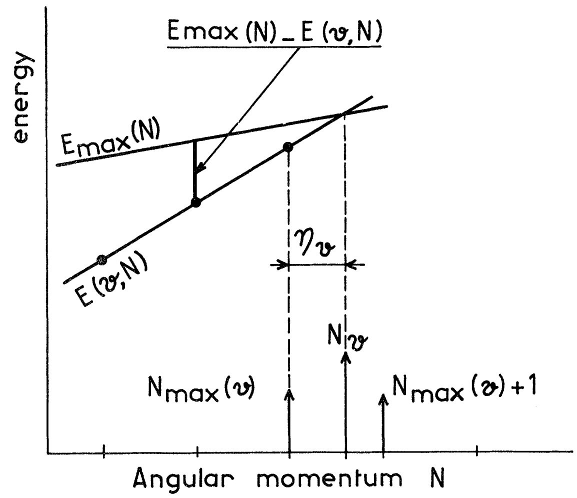

FIG. 5. Structure of the molecular levels lying near the top of the centrifugal barrier: the heavy dots correspond to the position of the levels.

$$D(v,N)=\exp[-2\pi a_v(\eta_v+N_{\max}-N)]\ , \tag{32}$$

with

$$a_v\approx(\hbar\omega_N)^{-1}\left(\frac{d[E_{\max}(N)-E(v,N)]}{dN}\right)_{N=N_v}\ , \tag{33}$$

as one can deduce from Eqs. (28) and (31) using a Taylor expansion of $E_{\max}(N)$ and $E(v,N)$ around $N=N_v$. We give in Table II the values of a_v for the different vibrational numbers involved. An inspection of this table shows that D is extremely sensitive to the value of η_v. To know η_v within an error, say of 10^{-2}, implies that one has evaluated $E(v,N)$ with a precision of 10^{-3}, and this is probably not the case with our semiclassical approximation. Furthermore there is certainly some uncertainty in the determination of the Rb-Kr potential. So the only reasonable thing one can do is to derive upper and lower bounds for $D(v,N)$ from the inequality $0\leq\eta_v\leq 1$.

Finally, we would like to derive the probability per unit time to produce a Rb-Kr metastable state (v,N) in a two-body collision. The cross section for the value E of the relative energy is given by the well-known Breit-Wigner formula

$$\sigma_{v,N}(E)=\frac{\pi\lambda\!\!\!^{-2}(2N+1)\Gamma^e(v,N)\Gamma^t(v,N)}{[E-E(v,N)]^2+[\Gamma^t(v,N)/2]^2}\ , \tag{34}$$

with $\lambda\!\!\!^{-}=\hbar/(2\mu E)^{1/2}$; (35)

$$\Gamma^e(v,N)=\hbar/\tau^e(v,N)=\hbar D(v,N)/\tau_0$$

is the elastic width while $\Gamma^t(v,N)=\hbar/\tau^t(v,N)$ is the total width. The cross section has to be averaged over the thermal distribution $f(E)$ of the relative energy:

$$\sigma_{v,N}=\int\sigma_{v,N}(E)f(E)dE$$

$$\simeq\lambda_T^{\,3}(2N+1)[1/\tau^e(v,N)]$$

$$\times[\mu/2E(v,N)]^{\frac{1}{2}}e^{-\beta E(v,N)}\ . \tag{36}$$

The rate of formation $[T_f^{\,e}(v,N)]^{-1}$ is given by[15]

$$\frac{\tau^e(v,N)}{T_f^{\,e}(v,N)}=\lambda_T^{\,3}\mathcal{V}^{-1}N_{\mathrm{Kr}}(2N+1)e^{-\beta E(v,N)}$$

$$=N_{\mathrm{Kr}}\,\mathcal{P}(v,N)\ . \tag{37}$$

Note that the above formula is identical with the one obtained in the case of production of bound or metastable states in three-body collisions (see Eqs. 14 and 9). We can thus conclude that in the case of a metastable state the *total* formation and destruction rates $[T_f^{\,t}(v,N)^{-1}$ and $\tau^t(v,N)^{-1}]$ taking into account two-body *and* three-body processes also satisfy the relation

$$\tau^t(v,N)/T_f^{\,t}(v,N)=N_{\mathrm{Kr}}\,\mathcal{P}(v,N)\ , \tag{38}$$

as a consequence of thermal equilibrium.

Actually, it will be shown in Appendix B that resonant two-body collisions play a negligible role in the pressure range covered experimentally. They might become important in the relaxation process induced by "sticking" collisions only at pressures lower than 0.1 Torr.

TABLE II. The numerical value of $2\pi a_v$. For each vibrational number, the value of $2\pi a_v=\log\,[D(v,N-1)/D(v,N)]$ [see Eq. (32)] yields the ratio between the transmission coefficients D of metastable states (v,N) and $(v,N-1)$, both lying near the top of the centrifugal barrier.

v	0	1	2	3	4	5	6	7	8	9	10
$2\pi a_v$	2.4	2.7	3.0	3.6	3.8	3.2	3.3	3.6	4.0	6.5	12.5

IV. RELAXATION IN "SUDDEN" TWO-BODY COLLISIONS

The relaxation induced by the spin-orbit potential in "sudden" two-body collisions will be described by a stochastic Hamiltonian which we define now. Let us specify a collision by the impact parameter $\vec{b}$, the initial relative velocity $\vec{V}$ of the two colliding atoms, and the instant t_c when the distance r between the two atoms reaches its minimum. The interaction Hamiltonian appears as a function of the stochastic variables $\vec{b}$, $\vec{V}$, t_c:

$$\mathcal{H}_1(t-t_c,\vec{b},\vec{V}) = \hbar^{-1}\gamma(r(t-t_c))\vec{S}\cdot(\mu\vec{V}\times\vec{b}) , \tag{39}$$

where $r(t)$ is obtained by solving the classical equation of motion of the relative particle. We shall assume that the actual motion is not very different from that of two colliding hard spheres having a radius r_0

$$\begin{aligned} r(t) &= (b^2 + V^2t^2)^{1/2} , & b &\geq r_0 , \\ r(t) &= (r_0^2 + V^2t^2 + 2\sqrt{r_0^2 - b^2}\, V|t|)^{1/2} , & b &\leq r_0 . \end{aligned} \tag{40}$$

This assumption, which leads to tractable mathematical expressions, gives a reasonably good picture of the real motion: for small impact parameters attractive forces play no role and for large impact parameters where they are predominant the deflection angle is small and the trajectory looks like a straight line. The effective hard-sphere radius r_0 is obtained by comparing the distance of closest approach as a function of b (at a fixed value of the kinetic energy $\sim \frac{3}{2}kT$) for a hard sphere and for a 12-6 Lennard-Jones potential (see Fig. 6). One finds that r_0 is practically equal to the finite value of r at which the Lennard-Jones potential goes to zero, $r_0 \approx r_m/2^{1/6}$.

The probability that a Kr atom suffers a collision characterized by an impact parameter in the interval $\vec{b}, \vec{b}+d\vec{b}$, with an initial relative velocity in the interval $\vec{V}$, $\vec{V}+d\vec{V}$ within the time interval dt is given by

$$Vn(\vec{V})\,d^3V\,d^2b\,dt \quad ,$$

where $n(\vec{V})d^3V$ is the number of Kr atoms per unit volume with a relative velocity in the interval $\vec{V}, \vec{V}+d\vec{V}$.

Let us consider two eigenstates $|i\rangle$ and $|j\rangle$ of the static Hamiltonian $\mathcal{H}_0$ of the Rb atoms having an energy interval $\hbar\omega_{ij}$. The average transition probability in the time interval t, $t+\Delta t$ is given in first order perturbation theory by

$$\Delta W_{ij} = \hbar^{-2}\langle|\int_t^{t+\Delta t} dt'\, e^{i\omega_{ij}t'}\langle j|\mathcal{H}_1(t'-t_c,\vec{b},\vec{V})|i\rangle|^2\rangle_{\text{av}} . \tag{41}$$

The time interval Δt is small on the macroscopic scale, in particular much smaller than the time of flight τ_f, but large on the microscopic scale, i.e., much larger than the average duration of a disorienting interaction. For $t<t_c<t+\Delta t$, it is legitimate to replace the integration over the interval t, $t+\Delta t$ by one from $-\infty$ to $+\infty$. Using the probability law given above, ΔW_{ij} can then be written in the following form:

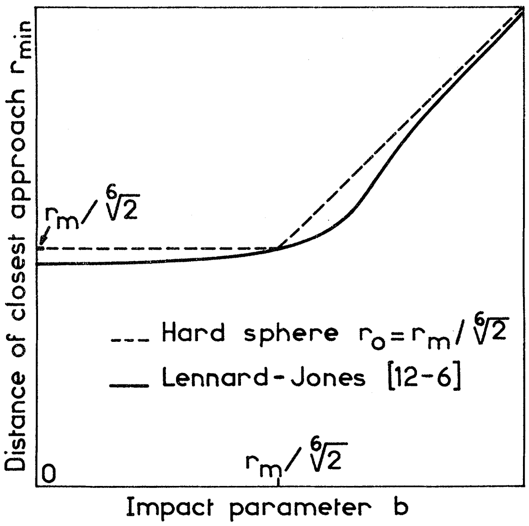

FIG. 6. Comparison between the distance of closest approach $r_{\min}$ as a function of the impact parameter b at a fixed value of the kinetic energy $(E=\frac{3}{2}kT=3.9\epsilon)$ for a Lennard-Jones 12-6 potential (ϵ, r_m) and for a hard-sphere potential of radius $r_0=r_m/2^{1/6}$.

$$\Delta W_{ij} = \Delta t \hbar^{-2} \int V n(\vec{V}) d^2 b\, d^3 V \left| \int_{-\infty}^{+\infty} e^{i\omega_{ij} t} \langle j | \mathcal{H}_1(t, \vec{b}, \vec{V}) | i \rangle dt \right|^2 . \tag{42}$$

The squared integral represents the Fourier transform of the correlation function of the ij matrix element of $\mathcal{H}_1$ taken at ω_{ij}.

The relaxation time of an alkali atom without nuclear spin is readily obtained:

$$T_{S1}^{-1} = 2\Delta W_{\frac{1}{2}, -\frac{1}{2}} / \Delta t = (\mu^2/3\hbar^4) \int V^3 b^2 n(\vec{V}) d^2 b\, d^3 V \left| \int_{-\infty}^{+\infty} e^{i\omega_0 t} \gamma(r(t)) dt \right|^2 . \tag{43}$$

If it were possible to study experimentally T_{S1}^{-1} as a function of the Larmor frequency ω_0, information on the shape of $\gamma(r)$ could be deduced. Unfortunately only the range $\omega_0 \times$average collision time $\ll 1$ is accessible to experiment so that we can put $\omega_0 = 0$ in the above formula (the exponential factor being practically 1 in all the domain where the expression to be integrated is not zero).

If, from the measured relaxation rate, one wants to deduce a value for the strength of the spin-orbit potential, one has to make a specific assumption about the shape of $\gamma(r)$. A theoretical analysis of the spin-orbit potential[5] indicates that the long-range part of $\gamma(r)$, due to van der Waals interactions, which behaves like r^{-2n} is probably much weaker than the short-range part associated with the repulsive electrostatic and exchange forces. In our analysis we have used for $\gamma(r)$ the following expression:

$$\gamma(r) = \gamma_a e^{-\kappa^2 (r^2 - r_0^2)} + \gamma_b (r_0/r)^{2n} . \tag{44}$$

The first term, coming from repulsive forces, has to be characterized by a range κ^{-1} small compared with r_0. For the second van der Waals term, arguments exist in favor of the value 8 for the exponent $2n$.[5] The effects of these two interactions may be considered separately, since one can easily show that the contribution of the cross term is very small. After lengthy computations one thus gets the following result:

$$T_{S1}^{-1} = \tau_f^{-1} (\mu^2 r_0^4/\hbar^4) [\gamma_a^2 F_a(\kappa r_0) + \gamma_b^2 F_b(n)] (r_0/r_m)^2 , \tag{45}$$

with

$$F_a(u) = \tfrac{2}{3}\pi \left\{ (u\sqrt{2})^{-4} + e^{2u^2} u^{-6} \int_0^u x^3 e^{-2x^2} \left[1 - (2/\sqrt{\pi}) \int_0^{(u^2 - x^2)^{1/2}} e^{-t^2} dt \right]^2 dx \right\} , \tag{46}$$

$$F_b(n) = \tfrac{4}{3} \left\{ C_n^2/(2n-3) + 2 \int_0^{\pi/2} (\sin u)^{5-4n} \cos u \left[\int_{\cot u}^{+\infty} (1+x^2)^{-n} dx \right]^2 du \right\} , \tag{47}$$

$$C_n = \int_0^{+\infty} (1+x^2)^{-n} dx = \frac{\pi}{2} \frac{1 \cdot 3 \cdot 5 \cdots (2n-3)}{2 \cdot 4 \cdot 6 \cdots (2n-2)} .$$

The numerical factors $F_a(\kappa r_0)$ and $F_b(n)$ are typical of the *shape* of the spin-orbit potential. For $2n = 8$ one finds $F_b(n) = 0.105$. Some numerical values of $F_a(\kappa r_0)$ are readily obtained from Table III. $F_a(\kappa r_0)$ is a rapidly decreasing function of κr_0, due simply to the fact that the interaction duration is shorter the smaller the range of the spin-orbit potential. If the numerical factors $F_a(\kappa r_0)$ and $F_b(n)$ are taken separately, the above expression (45) is easily interpreted. Let us consider collisions occuring with an impact parameter of the order of r_0. The Hamiltonian is

$$\mathcal{H}_1 = \gamma(r) \vec{S} \cdot \vec{N} \sim \hbar^{-1} \gamma(r_0) \mu r_0 \bar{V}_r ,$$

the duration of the disorienting interaction is of the order of $\tau_{\text{coll}} = r_0 / \bar{V}_r$ and the collision frequency for a given Rb atom is

TABLE III. The numerical values of $\log_{10} [F_a(\kappa r_0)]^{-1}$.

κr_0	1.0	1.5	2.0	2.5	3.0	3.5	4.0
$-\log_{10} F_a(\kappa r_0)$	0.137	0.772	1.217	1.561	1.843	2.082	2.289
κr_0	4.5	5.0	5.5	6.0	6.5	7.0	8.0
$-\log_{10} F_a(\kappa r_0)$	2.472	2.637	2.786	2.923	3.049	3.167	3.383

$$\pi r_0{}^2 \overline{V}_r N_{\mathrm{Kr}} \mathcal{V}^{-1} = \tau_f{}^{-1}(r_0/r_m)^2 .$$

Using the above physical parameters, Eq. (45) can be rewritten and gives as an order of magnitude of the relaxation rate

$$T_{S1}{}^{-1} \sim \tau_f{}^{-1}(r_0/r_m)^2 \times [\gamma(r_0)\mu r_0 \overline{V}_r/\hbar^2]^2 \times (r_0/\overline{V}_r)^2 , \tag{48}$$

or

$$\text{relaxation rate} \sim \text{collision rate} \times \langle |\mathcal{H}_1|^2\rangle_{\mathrm{av}} \hbar^{-2} \times \tau^2_{\mathrm{coll}} .$$

This is simply a very familiar result of the relaxation theory valid in gases when the motional narrowing condition $\langle |\mathcal{H}_1|^2\rangle_{\mathrm{av}} \hbar^{-2}\tau^2_{\mathrm{coll}} \ll 1$ is fulfilled.[16] One can note also in Eq. (45) that the velocity dependence is the same for T_{S1} as for τ_f ; consequently one should observe experimentally that the disorienting cross section is velocity independent.

The effect of the nuclear spin I of the alkali atom can be taken into account. Using Eq. (42) one can compute $(4I+1)$ longitudinal relaxation times which are related to T_{S1} by simple geometrical factors involving only the nuclear multiplicity (see Ref. 6). For instance, the time evolutions of observables

$$\langle I_z\rangle, \quad \langle Q_e\rangle = \langle S_z\rangle - \{2/[(2I+1)^2-2]\}\langle I_z\rangle, \quad \text{and } \langle \vec{S}\cdot\vec{I}\rangle$$

are each pure exponentials characterized by the time constants T_n, T_e, T_{H} such that

$$[2/(2I+1)^2]\, T_n = T_e = T_{\mathrm{H}} = T_{S1} . \tag{49}$$

V. THEORY OF THE RELAXATION INDUCED BY COLLISIONS LEADING TO BOUND AND METASTABLE STATES

In the preceding section we have obtained the rate of relaxation induced by "sudden" two-body collisions, by making use of the assumption that the disorientation probability for a single collision is smaller than unity (the motional narrowing condition applies). This condition is not always satisfied when one deals with the relaxation induced by "sticking" collisions. This comes from the fact that at low pressures, the collision lifetime of a molecular state becomes long enough to allow $\vec{S}$ and $\vec{N}$ to couple together and to precess around their resultant, to such an extent that the initial orientation of $\vec{S}$ is completely lost when the molecule gets destroyed. For this reason we would like to present now a derivation of the master equation for the relaxation of Rb atoms induced by this second mechanism, a derivation which is valid whether or not the motional narrowing condition be satisfied.

A. Model Specification

First of all, we shall assume that the first collision undergone by a Rb-Kr molecule immediately after its production either breaks the molecule or leaves it with its orbital angular momentum unchanged. The case of collisions inducing transitions between states of different orbital angular momentum, for which we have not been able to perform a rigorous theoretical treatment, will be only briefly discussed at the end of the present section (part E).

To avoid unessential complications we shall ignore the effect of the nuclear spin. Its inclusion does not raise special difficulties and the corresponding results will be given without the detailed proof.

The spin-dependent Hamiltonian in a Rb-Kr molecule is written as

$$\mathcal{H} = \gamma_S \vec{S}\cdot\vec{H}_0 + \gamma\vec{S}\cdot\vec{N} . \tag{50}$$

The first term represents the interaction of the valence electron with a static external magnetic field $\vec{H}_0$. The second term is the spin-orbit coupling. The coefficient γ is the average value of $\gamma(r)$ for a given state (v, N). We shall neglect the dependence of γ upon the vibrational number and express all results by taking the average over the different molecular states. Furthermore we shall treat $\vec{N}$ as a fixed vector during the lifetime of the molecule. This assumption needs obviously some justification. Although one can show easily that in many circumstances the variation of $\vec{N}$ under the influence of $\mathcal{H}$ is indeed negligible there are at least a few instances in which this is not true. However, a rigorous analysis can be performed; it leads practically to the same result as the approximate treatment given below, as is shown in Appendix A.

The spin-orbit interaction has the same effect as an external magnetic field $\vec{H}_1 = (\gamma/\gamma_S)\vec{N}$ and we shall rewrite $\mathcal{H}$ as

$$\mathcal{H} = \gamma_S \vec{S} \cdot \vec{H} \ , \tag{51}$$

$$\vec{H} = \vec{H}_0 + \vec{H}_1 \ . \tag{52}$$

During the formation of a molecular state the magnetic field acting on $\vec{S}$ jumps from the value $\vec{H}_0$ to the value $\vec{H}$ in a time of the order of 10^{-12} sec, short enough for the sudden approximation to be valid. The stochastic magnetic field acting on a given Rb atom is shown in a schematic way in Fig. 7.

At instant t_0 the Rb atom is captured by a Kr atom in a three-body collision to form a molecular state, destroyed at instant $t_0 + T$. The same process occurs again at some instant t_0' later with an uncorrelated value of H_1. The stochastic variable T is governed by the exponential law

$$\text{Probability}\,(t \leq T \leq t + dt) = e^{-t/\tau} dt/\tau, \tag{53}$$

where τ is the collision lifetime of the molecular state (τ is assumed to be the same for all the molecular states involved). The probability that a "sticking" collision occurs for a given Rb atom in the interval $(t_0, t_0 + dt)$ is dt/T_f. For the pressure range of Kr explored relations (11) and (15) show that T_f is always much larger than τ.

We shall now proceed to the derivation of the relaxation equation for the average polarization $\langle S_z \rangle$ of an ensemble of Rb atoms subjected to the stochastic interaction we have just described.

B. Derivation of the Relaxation Equation for $\langle S_z \rangle$

Let us consider the evolution of our ensemble over a time interval Δt chosen as follows: Δt is much larger than the lifetime of the molecular states and much smaller than T_f the mean time interval between two "sticking" collisions suffered by a given Rb atom. Let us now separate the Rb atoms into two classes: (a) the fraction $\Delta t/T_f$ of Rb atoms which get bound to a Kr atom during the time interval Δt; (b) the fraction $1 - \Delta t/T_f$ of those which remain free during the same time interval.

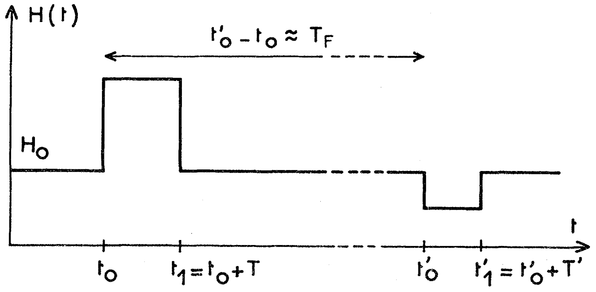

FIG. 7. Schematic representation of the random time-dependent magnetic field acting upon a given Rb atom.

We neglect the atoms which participate twice or more in a molecular state, as well as those which are engaged in a molecular state at the instants t or $t + \Delta t$, since they constitute a very small fraction of the total number [respectively of the order of $(\Delta t/T_f)^2$ and $2\tau/T_f$].

Let $\Psi(t)$ be the wave function of an atom of class (a) at instant t. Between t and t_0 the evolution of $\Psi(t)$ is governed by the Hamiltonian $\mathcal{H}_0 = \gamma_S \vec{S} \cdot \vec{H}_0$, between t_0 and $t_0 + T$ by $\mathcal{H} = \gamma_S \vec{S} \cdot (\vec{H}_0 + \vec{H}_1)$, and between $t_0 + T$ and $t + \Delta t$ by $\mathcal{H}_0$ again. The final state $\Psi(t + \Delta t)$ is given by

$$\Psi(t + \Delta t) = \mathfrak{U}(t_0, T, \vec{H}_1)\Psi(t) \ , \tag{54}$$

with
$$\mathfrak{U}(t_0, T, \vec{H}_1) = e^{-i\hbar^{-1}\mathcal{H}_0(t + \Delta t - t_0 - T)} \times e^{-i\hbar^{-1}\mathcal{H}T} e^{-i\hbar^{-1}\mathcal{H}_0(t_0 - t)} \ . \tag{55}$$

We have written explicitly in $\mathfrak{U}$ the dependence upon the stochastic variables t_0, T, and $\vec{H}_1$. Two kinds of average have to be performed: one over the initial conditions, and the other over the stochastic variables t_0, T, and $\vec{H}_1$. The first one is done by describing the initial state of our ensemble of atoms by a density matrix $\rho_{mn}(t)$ written in the basis which diagonalizes $\mathcal{H}_0$. We shall restrict our investigation to the case in which $\rho_{mn}(t)$ is diagonal:

$$\rho_{mn}(t) = P_m(t)\delta_{mn} \ . \tag{56}$$

The density matrix of atoms of class (b) remains constant in time, while the one of atoms of class (a) is subjected to an evolution governed by the matrix $\mathfrak{U}$ suitably averaged. The density matrix of the whole ensemble is given at time $t + \Delta t$ by

$$\rho(t + \Delta t) = (1 - \Delta t/T_f)\rho(t) + (\Delta t/T_f)\langle \mathfrak{U}\rho(t)\mathfrak{U}^\dagger \rangle_{\text{av}} \ . \tag{57}$$

Using the fact that $\rho(t)$ is diagonal an equivalent way to write this is

$$\rho_{mn}(t + \Delta t) - \rho_{mn}(t) = (\Delta t/T_f) \times [-\delta_{m,n} P_m(t) + \textstyle\sum_{m'} \langle \mathfrak{U}_{m'} \mathfrak{U}^*_{nm'} \rangle_{\text{av}} P_{m'}(t)]. \tag{58}$$

We shall first show that

$$\langle \mathfrak{U}_{m'} \mathfrak{U}^*_{nm'} \rangle_{\text{av}} = \langle |\mathfrak{U}_{mm'}|^2 \rangle_{\text{av}} \delta_{m,n} \ . \tag{59}$$

Indeed, let us write the explicit dependence of $\mathfrak{U}_{mm'}$, $\mathfrak{U}^*_{nm'}$ upon the azimuthal angle ϕ of $\vec{H}_1$ with respect to $\vec{H}_0$ (see Fig. 8)

$$\mathfrak{U}_{mm'}(\phi)\mathfrak{U}^*_{nm'}(\phi)$$

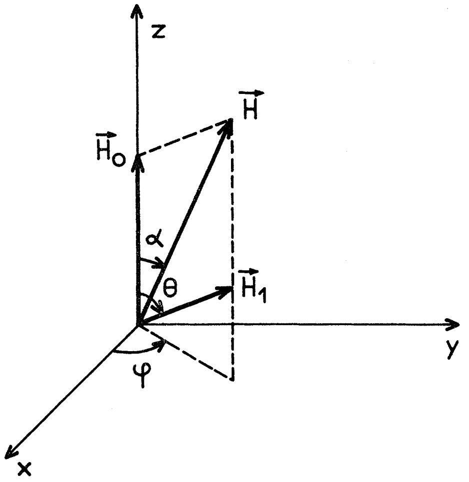

FIG. 8. Relative orientation of the steady field $\vec{H}_0$, the random field $\vec{H}_1$ unity, and the resultant field $\vec{H}$ acting on a Rb atom which is engaged in a Rb-Kr molecule.

$$= e^{i(m-n)\phi}\mathcal{U}_{mm'}(0)\mathcal{U}^*_{nm'}(0) \ . \qquad (60)$$

The average over ϕ gives

$$\langle e^{i(m-n)\phi}\rangle_{\text{av}} = \delta_{m,n} \ .$$

It then follows that $\rho_{mn}(t+\Delta t)$ remains diagonal.

Rewriting Eq. (58) in terms of the populations $P_m(t)$ we obtain

$$P_m(t+\Delta t) - P_m(t) = -(\Delta T/T_f)\textstyle\sum_{m'}[\delta_{mm'} - \langle |\langle m| e^{-i\hbar^{-1}\mathcal{H}T}|m'\rangle|^2\rangle_{\text{av}}]P_{m'}(t) \ . \qquad (61)$$

Since we have chosen $\Delta t/T_f \ll 1$, the variation of $P_m(t)$, between t and $t+\Delta t$ is very small. We are now in position to write the master equations for the population $P_m(t)$:

$$dP_m(t)/dt = -T_f^{-1}\textstyle\sum_{m'}[\delta_{m,m'} - \langle |\langle m| e^{-i\hbar^{-1}\mathcal{H}T}|m'\rangle|^2\rangle_{\text{av}}]P_{m'} \ . \qquad (62)$$

From this equation we can deduce immediately the relaxation equation of the electronic polarization $\langle S_z\rangle$

$$d\langle S_z\rangle/dt = -T_S^{-1}\langle S_z\rangle \ , \qquad (63)$$

with $T_S^{-1} = 2T_f^{-1}$

$$\times\langle |\langle -\tfrac{1}{2}| e^{-i\hbar^{-1}\gamma_S \vec{S}\cdot\vec{H}T}|\tfrac{1}{2}\rangle|^2\rangle_{\text{av}} \ . \qquad (64)$$

C. Explicit H_0 and P Dependences of the Relaxation Rate

We have now to perform the average over T and $\vec{H}_1$. It is convenient to introduce the following quantities: α, the angle between $\vec{H}_0$ and $\vec{H}$; θ, the angle between $\vec{H}_0$ and $\vec{H}_1$;

$$\hbar\omega = \gamma_S H; \quad \hbar\omega_0 = \gamma_S H_0; \quad \hbar\omega_1 = \gamma_S H_1 \ . \qquad (65)$$

Using simple identities involving Pauli matrices, we obtain the following simple expression for T_S:

$$T_S^{-1} = 2T_f^{-1}\langle \sin^2\alpha \sin^2\tfrac{1}{2}\omega T\rangle_{\text{av}} \ . \qquad (66)$$

The average over T is performed readily:

$$\int(\sin^2\tfrac{1}{2}\omega T)\mathcal{P}(T)dT = \tfrac{1}{2}\omega^2\tau^2/(1+\omega^2\tau^2) \ . \qquad (67)$$

After a few manipulations we arrive at the final expression

$$T_S^{-1} = T_f^{-1}\int d(\cos\theta)\mathcal{P}(\omega_1)d\omega_1 \times \frac{\omega_1^2\tau^2\sin^2\theta}{1+(\omega_0^2+\omega_1^2+2\omega_0\omega_1\cos\theta)\tau^2} \ . \qquad (68)$$

Remembering the definition of ω_1 [Eq. (65)], the distribution $\mathcal{P}(\omega_1)$ is obtained from the knowledge of the probability $\mathcal{P}(N)$ of finding a Rb-Kr molecule in a state of orbital momentum N

$$\mathcal{P}(N) \propto \sum_{v\leqslant v_{\max}(N)} (2N+1)e^{-\beta E(v,N)} \ .$$

The discrete law of probability $\mathcal{P}(N)$ shown in Fig. 9 can be approximated by the following con-

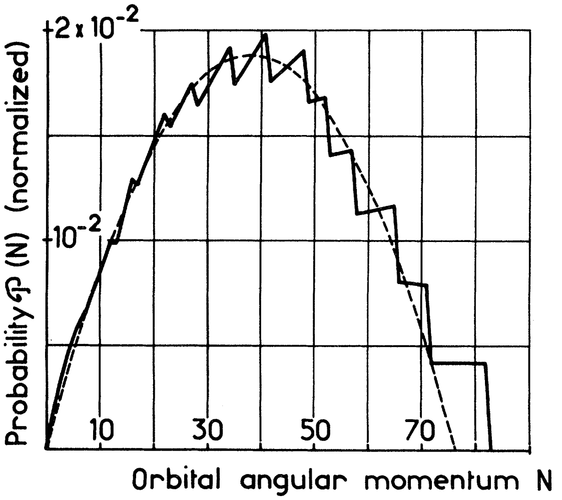

FIG. 9. Law of probability for finding a Rb-Kr molecule in a state of orbital angular momentum N:

$$\mathcal{P}(N) = \sum_{v\leqslant v_{\max}(N)} \mathcal{P}(v,N) \Big/ \sum_{v,N} \mathcal{P}(v,N) \ .$$

The dashed parabola stands for the approximate distribution used for averaging results over N.

tinuous law:

$$\mathcal{P}(N)dN = (3/4\overline{N}^3)N(2\overline{N} - N)dN, \quad 0 \leq N < 2\overline{N}$$
$$0 \ , \qquad N > 2\overline{N}$$

with $2\overline{N} = 76$. (69)

The average over $\cos\theta$ can still be performed analytically, but the final average over ω_1 has been done by numerical integration. The result depends essentially on $\langle\omega_1{}^2\rangle_{\mathrm{av}}$, which we shall write explicitly as a function of the spin-orbit potential. Let us define $\overline{\gamma}$ such that

$$\langle N(N+1)\rangle_{\mathrm{av}}\overline{\gamma}^2 = \sum_{v,N} \mathcal{P}(v,N)N(N+1) \times \frac{\left[\int dr|y_{v,N}(r)|\right]^2}{\sum_{v,N} \mathcal{P}(v,N)} , \tag{70}$$

$r^{-1}y_{v,N}(r)$ being the radial wave function of the molecular state (v,N). We find

$$\langle\omega_1{}^2\rangle_{\mathrm{av}} = \langle N(N+1)\rangle_{\mathrm{av}}\overline{\gamma}^2\hbar^{-2} \ . \tag{71}$$

The lifetime τ should vary from one molecular state to another. Since no precise estimate of the break-up cross-section is possible, we have decided to ignore this variation, and we write for the destruction rate τ^{-1} and the associated (see Eq. 15) formation rate

$$\tau^{-1} = N_{\mathrm{Kr}}\mathfrak{V}^{-1}V_{Mr}\overline{\sigma} = \beta P\overline{V}_{Mr}\overline{\sigma} \ , \tag{72}$$

$$T_f{}^{-1} = \overline{V}_{Mr}(\beta P)^2\mathcal{K}\overline{\sigma} \ , \tag{73}$$

where $\overline{\sigma}$ is an average cross section, $\mathcal{K}$ is the equilibrium constant. $V_{Mr} = V_r\sqrt{3}/2$ is the average thermal relative velocity of a Rb-Kr molecule and a Kr atom, and $\beta = (kT)^{-1}$. We neglect here the formation of metastable states by two-body resonant collisions. This mechanism is discussed in Appendix B and shown to be of no practical importance in the pressure range covered experimentally.

The functional dependence of T_S upon P and H_0 is then defined by the three phenomenological parameters $\mathcal{K}$, $\overline{\sigma}$, and $\overline{\gamma}$. We would like to discuss first the general expression of T_S for some particular cases:

(1) $\omega_1\tau \ll 1$. This is the so-called "motion narrowing condition." The two averages are performed readily

$$T_S{}^{-1} = \tfrac{2}{3}T_f{}^{-1}\langle\omega_1{}^2\rangle_{\mathrm{av}}\tau^2/(1 + \omega_0{}^2\tau^2) \ . \tag{74}$$

This result is identical to the one which would be obtained by using the general perturbation theory of relaxation. The relaxation rate varies with the Larmor frequency as the Fourier transform of the correlation function of the perturbation.

(2) $\omega_1 \gg \omega_0$, $\omega_1\tau \gg 1$. We have to deal with "strong collisions"

$$T_S{}^{-1} = \tfrac{2}{3}T_f{}^{-1} \ . \tag{75}$$

The dependence upon ω_0 disappears as one might expect, since the initial orientation of the electronic spin gets lost each time a Rb atom suffers a "sticking" collision (unless $\vec{H}_1$ be parallel to $\vec{H}_0$).

(3) $\omega_0 \gg \omega_1$, $\omega_1\tau \gg 1$. The electronic spin $\vec{S}$ is partially decoupled from $\vec{H}_1$, i.e., the large dc field H_0 decouples angular momenta $\vec{S}$ and $\vec{N}$:

$$T_S{}^{-1} = \tfrac{2}{3}T_f{}^{-1}\langle\omega_1{}^2\rangle_{\mathrm{av}}/\omega_0{}^2 \ . \tag{76}$$

D. Effects of the Alkali Nuclear Spin

We shall now state the results which are valid when the alkali nuclear spin I is taken into account. We suppose the dc field H_0 so small that the Zeeman splitting remains much smaller than the hyperfine structure. Collisions leading to Rb-Kr molecular states have a negligible effect on the time evolution of observable $\vec{S}\cdot\vec{I}$. This result is the consequence of two facts: (1) the interaction $\gamma_S\vec{S}\cdot\vec{H}_1$ is weak compared to the hyperfine coupling; (2) the lifetime of the molecular states is very large compared to the reciprocal of the hyperfine frequency. The time evolutions of observables $\langle S_z\rangle$ and $\langle I_z\rangle$ are identical, and the relaxation rates $T_n{}^{-1} = T_e{}^{-1}$ are given by the expression (68) with the following definitions of ω_0 and ω_1:

$$|\omega_0| = \gamma_S H_0/(2I+1)\hbar \ ,$$
$$|\omega_1| = \gamma N/(2I+1)\hbar \ . \tag{77}$$

Let us then describe briefly the main features of the variation of T_n versus P and H_0 in the general case.

As a function of H_0, the quantity $T_n{}^{-1}$ can always be represented to good approximation by a Lorentzian curve:

$$A/[1 + (H_0/\Delta H_0)^2] \ . \tag{78}$$

In Fig. 10 we have represented the extreme case $P = 0$ when the deviation from an exact Lorentzian is *maximum*. We conclude that such a deviation cannot be observed experimentally. The P dependence of the parameters of the Lorentz curve ΔH_0 and A, which will play an essential role in the interpretation of the experimental results, can be conveniently expressed as follows:

$$A = A^*f(P/P^*) \ , \tag{79}$$

$$\Delta H_0 = H_1{}^*g(P/P^*) \ . \tag{80}$$

The functions f and g are represented in Figs. 11 and 12. The three parameters A^*, P^*, $H_1{}^*$ are given in terms of $\overline{\gamma}$, $\overline{\sigma}$, and $\mathcal{K}$ by

$$H_1{}^* = [(2I+1)\hbar/\gamma_S](\langle\omega_1{}^2\rangle_{\mathrm{av}})^{1/2} \ , \tag{81}$$

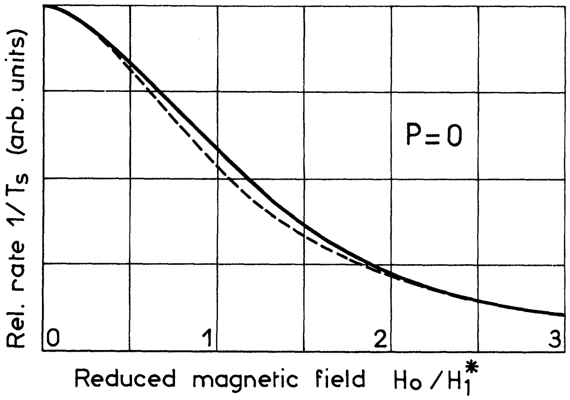

FIG. 10. Theoretical curve illustrating the field variation of the relaxation rate induced by "sticking" collisions. The curve is drawn in the limit case $P=0$ (meaning $P/P^* \ll 1$) and compared with a Lorentz curve (dashed).

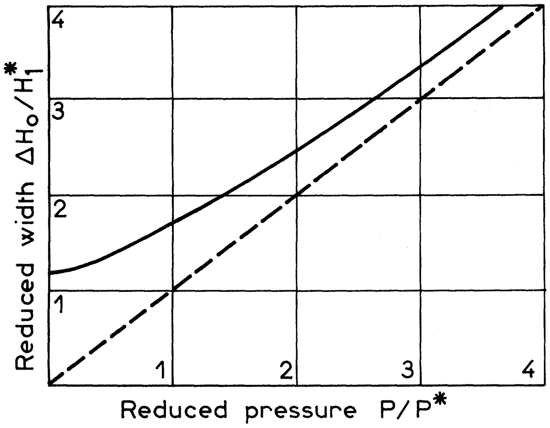

FIG. 12. Pressure dependence of the steady-field value in which the relaxation rate induced by three-body collisions leading to bound and metastable states, is twice smaller than in zero field: theoretical curve $\Delta H_0 = H_1^* g(P/P^*)$ with reduced units defined by Eqs. (81) and (83).

[or $H_1^* = (\frac{6}{5})^{1/2} \bar{\gamma} \bar{N} / \gamma_S$, (82)

using the distribution $\wp(N)$ described by Eq. (69)],

$$P^* = \gamma_S H_1^* / (2I+1) \hbar \beta \bar{V}_{Mr} \bar{\sigma} \ , \tag{83}$$

$$A^* = \tfrac{2}{3} \mathcal{K} \gamma_S{}^2 H_1^{*2} / (2I+1)^2 \hbar^2 \bar{V}_{Mr} \bar{\sigma} \ . \tag{84}$$

These parameters have simple physical interpretations: H_1^* is the root-mean-square value of the effective magnetic field simulating the spin-orbit interaction; P^* is the pressure at which the average lifetime $\bar{\tau}$ is equal to $(2\pi)^{-1}$ times the Larmor period of $\vec{F} = \vec{S} + \vec{I}$ in the field H_1^*; A^* is the asymptotic value of A at high pressures where, the motional narrowing condition $\omega_1{}^2 \tau^2 \ll 1$ is fulfilled.

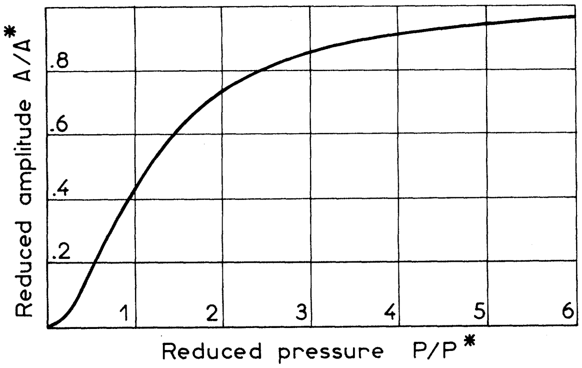

FIG. 11. Pressure dependence of the relaxation rate induced in zero field by three-body collisions leading to bound and metastable molecular states: theoretical curve $A = A^* f(P/P^*)$ with reduced units defined by Eqs. (83), (84).

E. Effects of Molecular Inelastic Collisions

We shall now discuss the modifications to the present theory, which might come from collisions inducing transitions between molecular states of different orbital angular momentum. Let us define two collision rates and their corresponding cross sections:

$$\tau_{tr}{}^{-1} = \beta P \bar{V}_{Mr} \sigma_{tr} \ , \tag{85}$$

$$\tau_b{}^{-1} = \beta P \bar{V}_{Mr} \sigma_b \ . \tag{86}$$

τ_{tr} represents a phenomenological correlation time for the relaxation process and τ_b the mean lifetime of a molecular state. σ_{tr} is of the order of the cross section associated either with a break-up of the molecule or an excitation with $\Delta N/\bar{N} > 0.1$ (Eq. 23), and σ_b is the break-up cross section. From the theoretical considerations of Sec. III it follows that the ratio σ_{tr}/σ_b probably lies between 1 and 3. Note that the formation rate is still related to $\tau_b{}^{-1}$ or σ_b by the expressions

$$T_f{}^{-1} = \mathcal{K} \beta P \tau_b{}^{-1} = \mathcal{K} (\beta P)^2 \bar{V}_{Mr} \sigma_b \ . \tag{87}$$

It is no longer possible to give a complete treatment of the relaxation problem for any value of P, but the following results can be easily obtained in the two extreme pressure ranges. In the high pressure range, the motion-narrowing condition $\langle \omega_1{}^2 \rangle_{\mathrm{av}} \tau_{tr}{}^2 \ll 1$ is fulfilled and $T_n{}^{-1}$ is given by

$$T_n{}^{-1} = \frac{2}{3} \frac{\tau_b}{T_f} \frac{\langle \omega_1{}^2 \rangle_{\mathrm{av}} \tau_{tr}}{1 + \omega_0{}^2 \tau_{tr}{}^2} \ . \tag{88}$$

The asymptotic expressions for $A(P)$ and $\Delta H_0(P)$ are unchanged provided we replace $\bar{\sigma}$ by σ_{tr} in A^* and P^*. In the low pressure range, $\langle\omega_1^2\rangle_{av} \times\tau_{tr}^2 \gg 1$, the quantity T_n^{-1} should read

$$T_n^{-1} = \tfrac{2}{3} T_f^{-1}, \qquad \text{if } \omega_0^2 \ll \langle\omega_1^2\rangle_{av} \tag{89}$$

and

$$T_n^{-1} = \tfrac{2}{3} T_f^{-1} \frac{\langle\omega_1^2\rangle_{av}}{\omega_0^2} \text{ if } \omega_0^2 \gg \langle\omega_1^2\rangle_{av} \tag{90}$$

The low-pressure limit of $A(P)$ is multiplied by the factor σ_b/σ_{tr}

$$A(P) = A^*(P/P^*)^2 \sigma_b/\sigma_{tr} \ , \tag{91}$$

while that of ΔH_0 is unchanged.

So, finally, we have at our disposal two possible ways of analyzing the data: (a) a three-parameter fit ($\bar{\gamma}$, $\bar{\sigma} = \sigma_{tr} = \sigma_b, \mathcal{K}$) where the full range of variation of P can be used, (b) a four-parameter fit ($\bar{\gamma}$, σ_{tr}, σ_b, $\mathcal{K}$) where only the results of the two extreme ranges are analyzed.

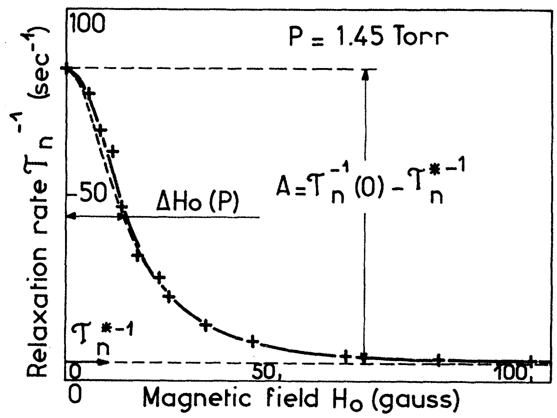

FIG. 13. Typical experimental data illustrating the field variation of the relaxation rate at a given Kr pressure (P = 1.45 Torr). The solid line is a fit to experimental data, the dashed curve is the result of a best fit performed with a Lorentz curve having amplitude $A(P)$ and half width $\Delta H_0(P)$.

VI. INTERPRETATION OF THE EXPERIMENTAL RESULTS

We are going to show now that the theoretical analysis developed in the previous sections allows an interpretation of the relaxation experiments performed on Rb undergoing collisions with Kr.[1] Two Rb isotopes ^{87}Rb ($I = \frac{3}{2}$) and ^{85}Rb ($I = \frac{5}{2}$) have been studied experimentally. The time evolution of $\langle S_z\rangle$ is found to involve two exponentials, the time constants of which will be called $\mathcal{T}_n$ and $\mathcal{T}_e$ ($\mathcal{T}_n > \mathcal{T}_e$). The time evolution of $\langle\vec{S}\cdot\vec{I}\rangle$ is a single exponential with time constant $\mathcal{T}_H$. $\mathcal{T}_n^{-1}$ and $\mathcal{T}_e^{-1}$ are strongly field-dependent, between 0.1 and 200 G. $\mathcal{T}_H^{-1}$ is not. Let us call $\mathcal{T}_n^{*-1}$ and $\mathcal{T}_e^{*-1}$ the "high"-field values, i.e., the plateau in the field dependence of $\mathcal{T}_n^{-1}$ and $\mathcal{T}_e^{-1}$ (see Fig. 13). We are going to compare $\mathcal{T}_n^{-1}(P, H_0) - \mathcal{T}_n^{*-1}(P)$ and $\mathcal{T}_e^{-1}(P, H_0) - \mathcal{T}_e^{*-1}(P)$ on the one hand, and $\mathcal{T}_n^{*-1}(P)$, $\mathcal{T}_e^{*-1}(P)$ and $\mathcal{T}_H^{-1}(P)$ on the other hand, with the theoretical relaxation rates of observables $\langle I_z\rangle$, $\langle Q_e\rangle$, and $\langle\vec{S}\cdot\vec{I}\rangle$ induced by the *two* uncorrelated relaxation processes just analyzed. "Sticking" collisions are responsible for the rapid field variation of $\mathcal{T}_n^{-1}$ and $\mathcal{T}_e^{-1}$, while "sudden" two-body collisions account for $\mathcal{T}_H^{-1}$ and the "high"-field values of $\mathcal{T}_n^{-1}$ and $\mathcal{T}_e^{-1}$.

A. Interpretation of the Field-Dependent Part of the Relaxation Rates

We first deal with

$$\mathcal{T}_n^{-1}(P, H_0) - \mathcal{T}_n^{*-1}(P)$$

For a fixed value of P, the H_0 dependence of the relaxation rate $\mathcal{T}_n^{-1}$ is represented to a good approximation by a Lorentz curve (Fig. 13). We define the amplitude of this curve,

$$A(P) = \mathcal{T}_n^{-1}(P, H_0) - \mathcal{T}_n^{*-1}(P) ,$$

and its half width measured at half amplitude $\Delta H_0(P)$ in the same way as we did for the theoretical relaxation rate $T_n^{-1}(P, H_0)$ (Sec. V, part D). A and ΔH_0 have been measured systematically for both ^{85}Rb and ^{87}Rb as a function of P; the points of Figs. 14 and 15 illustrate the results. At first sight the general features of the theoretical curves (Figs. 11 and 12) can be recognized. Moreover, simple relations predicted by the theory are found to be satisfied within experimental uncertainties, e.g.,

$\Delta H_0(P)$ and $A(P)$ independent of I at low pressure,

$$\left.\begin{array}{l} A(P) \propto 1/(2I+1)^2, \\ \Delta H_0(P) \propto (2I+1). \end{array}\right\} \text{ at high pressure.}$$

We can then proceed to the determination of the parameters giving the best agreement between theory and experiment. We are going to try the two possible fits described at the end of Sec. V:

(1) The results of the three-parameter fit are illustrated by the curves of Figs. 13 and 14. The corresponding values of the parameters H_1^*, P^*, A^* are

$$H_1^* = 9.35\ \text{G},$$
$$4P^*(^{87}\text{Rb}) = 6P^*(^{85}\text{Rb}) = 10.6\ \text{Torr},$$
$$16A^*(^{87}\text{Rb}) = 36A^*(^{85}\text{Rb}) = 6.26\times10^3\ \text{sec}^{-1} .$$

From these values, using formulas (82), (83), and (84), we deduce

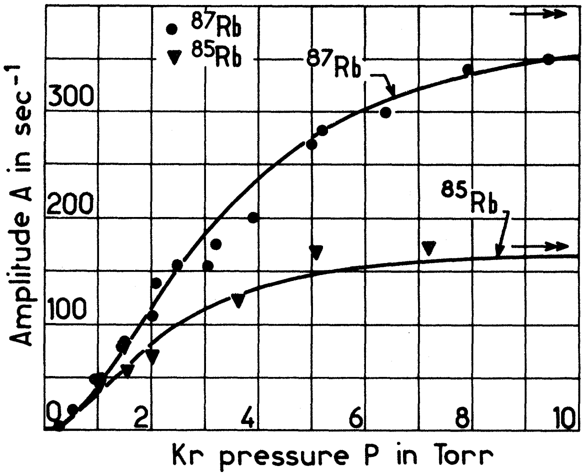

FIG. 14. Pressure variation of the field-dependent part of the relaxation rate A. Experimental points and theoretical curve (three-parameter fit).

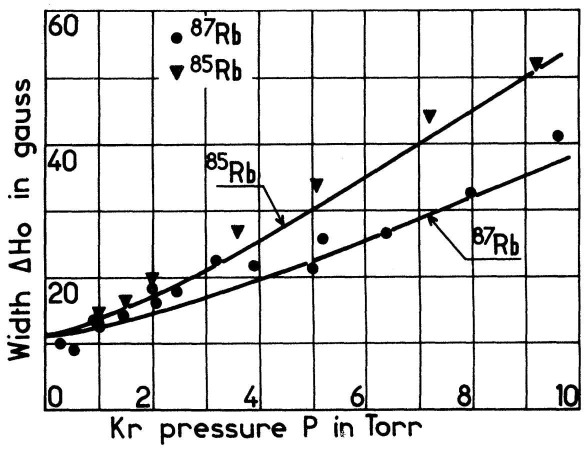

FIG. 15. Pressure variation of the parameter ΔH_0 defined on Fig. 13. Experimental points and theoretical curve (three-parameter fit).

$$\bar{\gamma}/h = 0.63 \text{ Mhz}, \quad \bar{\sigma} = 2.23\pi r_m{}^2,$$

$$\mathcal{K} = 1.68\times 10^{-22} \text{ cm}^3/\text{molecule}.$$

The corresponding destruction and formation rates for $P = 1$ Torr are

$$\tau^{-1} = 1.55\times 10^{7} \text{ sec}^{-1}, \quad T_f{}^{-1} = 84 \text{ sec}^{-1}.$$

The fraction of Rb atoms engaged in a bound Rb-Kr is then found to be

$$N_{\text{Kr-Rb}}/N_{\text{Rb}} = \tau/T_f = 5.4\times 10^{-6}P, \quad (P \text{ in Torr}).$$

(2) The four-parameter fit, which unfortunately relies on the experimental data obtained at the lowest and highest pressures, gives

$$H_1{}^* = 9.35 \text{ G}, \quad (2I+1)P^* = 9.5 \text{ Torr},$$

$$(2I+1)^2A^* = 6.26\times 10^3 \text{ sec}^{-1},$$

leading to

$$\bar{\gamma}/h = 0.63 \text{ Mhz}, \quad \sigma_{\text{tr}} = 2.5\pi r_m{}^2,$$

$$\mathcal{K} = 1.88\times 10^{-22} \text{ cm}^3/\text{molecule}, \quad \sigma_{\text{tr}}/\sigma_b = 1.25.$$

The value obtained for $\bar{\gamma}$ will be discussed later on; $\bar{\sigma}$ and σ_{tr} have the right order of magnitude (see Sec. III, part E). One can see from Figs. 12 and 13 that a fairly good account of experimental results is obtained within the assumption $\sigma_{\text{tr}}/\sigma_b = 1$. However most of experimental points of Fig. 15 lie above the theoretical curve, and this may be an indication of the fact that $\sigma_{\text{tr}}/\sigma_b$ is slightly different from 1 as it is suggested by the less precise four-parameter fit.

The value obtained for $\mathcal{K}$ is larger than the calculated value by a factor 1.15 to 1.3. The agreement can be considered as satisfactory if one bears in mind the experimental errors and the uncertainties affecting the shape of the Rb-Kr potential.[17]

B. Interpretation of the "High"-Field Values of the Relaxation Rates

We are now concentrating our interest on $\mathcal{T}_n{}^{*-1}(P)$, $\mathcal{T}_e{}^{*-1}(P)$, and $\mathcal{T}_H{}^{-1}(P)$, which we shall interpret in terms of the relaxation rates induced by the spin-orbit interaction during "sudden" two-body collisions.

$\mathcal{T}_n{}^{*-1}(P)$, $\mathcal{T}_e{}^{*-1}(P)$, and $\mathcal{T}_H{}^{-1}(P)$ have been measured for both isotopes; they are linear functions of P. The slopes obtained for the experimental straight lines are compared, in Table I, with the expected theoretical values given by Eq. (49). One can see that the agreement is quite good. Taking an average over all experimental results, one can deduce what would be the relaxation rate induced by "sudden" two-body collisions for a Rb isotope without nuclear spin, at a Kr pressure of 1 Torr

$$\mathcal{T}_{S1}{}^{-1} = \tfrac{1}{2}(2I+1)^2\, \mathcal{T}_n{}^{*-1} = \mathcal{T}_H{}^{-1}$$

$$= \mathcal{T}_e{}^{*-1} = 32 \text{ sec}^{-1}.$$

C. Range of the Spin-Orbit Potential

Using the theory developed in Sec. IV, we have at our disposal new information concerning the spin-orbit potential $\gamma(r)$. Inserting the experimental value $\mathcal{T}_{S1}{}^{-1} = 32$ sec^{-1} in Eq. (45), we get a relation between parameters $\gamma_a, \gamma_b, \kappa, n$ defining the spin-orbit potential:

$$\gamma_a{}^2 F_a(\kappa r_0) + \gamma_b{}^2 F_b(n) = 10.5\times10^{12}\hbar^2 \text{ sec}^{-2} . \quad (92)$$

Another relation can be obtained from the parameter $\bar{\gamma}$ deduced from the analysis of the relaxation via bound-state formation and defined by Eq. (70). We shall write $\bar{\gamma}$ as

$$\bar{\gamma} = \xi\gamma(r_m) , \quad (93)$$

where ξ is a parameter of the order of unity depending on the shape of $\gamma(r)$. Thus the second relation reads

$$\bar{\gamma}^2 = \xi^2[\gamma_a e^{-\kappa^2(r_m{}^2 - r_0{}^2)} + \gamma_b (r_0/r_m)^{2n}]^2$$

$$= 0.403\times10^{12}\hbar^2 \text{ sec}^{-2} , \quad (94)$$

$$r_m/r_0 = 2^{1/6} .$$

Let us assume first $\gamma_a = 0$. Following Herman we shall take $n = 4$. The shape parameter ξ has been computed by replacing the expectation value of $\gamma(r)$ for the state v, N by the average of $\gamma(r)$ over the classical trajectory. We hope that the effects of the quantum oscillations, neglected here, average out when the sum over all molecular states is performed. One finds in this way $\xi = 0.55$. Then two values of $\gamma_b{}^2$ can be obtained from Eqs. (92) and (94); they differ by a factor of 10. So, the hypothesis of a spin-orbit potential with only a long-range part does not seem to agree with the experimental data.

Let us consider now the case $\gamma_a \neq 0$, $\gamma_b = 0$ and assume for a moment that $\xi = 1$. A solution of Eq. (92) and Eq. (94) is then obtained with $\hbar^{-1}\gamma_a = 35\times10^6$Hz and $\kappa r_0 = 4$. The value obtained for the range parameter κ looks reasonable. If one computes by the same semi-classical method as above the shape parameter ξ relative to this particular potential one gets $\xi = 0.92$, in agreement with our *a priori* assumption that $\xi = 1$.

A complete determination of γ_a, γ_b and κr_0 from Eqs. (92) and (94) is of course impossible. However, one finds $|\gamma_b/\gamma_a| \leq 0.3$ when $\kappa r_0 \geq 3$ and $|\gamma_b/\gamma_a| \leq 0.07$ when $\kappa r_0 \geq 4$. It must be noted that our separation between short-range and long-range spin-orbit potentials is in fact meaningful only if $\kappa r_0 > 2$ since for $\kappa r_0 = 2$ the slopes of the "short range" and "long range" potential curves become equal. So in conclusion $\gamma(r)$ appears to be predominantly short-range as was predicted by the theoretical analysis of Herman.[5]

CONCLUSION

The relaxation study of polarized alkali atoms in the ground state yields information about spin-dependent interactions between alkali atoms and diamagnetic atoms and molecules. The method is sensitive enough to detect effects of interactions as small as fractions of 10^{-7} eV, but only the gross structure of the interaction can be obtained through averaged physical parameters. We have shown that the relaxation in gas phase is strongly affected by the presence of chemically unstable molecules like Rb-Kr bound by van der Waals forces. We have developed a model of relaxation valid for any value of the probability of disorientation per collision leading to molecular states. The theoretical predictions agree well with experimental results. Besides constituting unambiguous evidence for alkali rare-gas molecules, the relaxation experiments yield the chemical equilibrium constant of the $\text{Rb} + \text{Kr} \rightleftarrows \text{Rb-Kr}$ reaction: $\mathcal{K} = 1.7\times10^{-22}$ cm^3/molecule (for $T = 300\,°\text{K}$). This number corresponds to a proportion of one bound Rb atom to 1.8×10^5 free Rb atoms when the Kr pressure is $P = 1$ Torr. One can also deduce an average lifetime of a molecule in gas phase, $\tau = 0.65\times10^{-7}P^{-1}$ sec (krypton pressure P in Torr). These values of $\mathcal{K}$ and τ compare favorably with the theoretical estimates given in this paper. In agreement with experimental findings, it is shown that the formation of metastable states in two-body resonant collisions plays a negligible role in the relaxation process, at least in the pressure range explored experimentally. Finally, by comparing the results concerning the strength of the spin-orbit interaction acting on a Rb atom in fast two-body collisions and in a bound Rb-Kr molecule, one may conclude that the spin-orbit potential is predominantly short-range, in agreement with the theoretical predictions of Herman. The average spin-orbit coupling constant in a Rb-Kr molecule $\bar{\gamma}h^{-1}$ is found equal to 0.63 Mhz.

ACKNOWLEDGMENTS

It is a pleasure to the authors to express their thanks to Professor J. Brossel for his constant interest during the course of this work and for reading the manuscript. Discussions with Professors P. Bender and P. Sabatier are also gratefully acknowledged.

APPENDIX A

In this Appendix we shall examine the validity of the approximation made in Sec. V where the evolution of the orbital angular momentum $\vec{N}$ due to $\vec{S}\cdot\vec{N}$ coupling was neglected during the lifetime of the molecule. We shall show that the exact treatment leads to the same result provided N is large compared to unity;

this condition holds in our case since the average value of N is about 40.

The proof below is valid for any value of the static external field. The nuclear spin of the alkali atom is assumed to be zero. During the lifetime of the molecule, the effective Hamiltonian acting on the angular momentum part of the molecular wave function is

$$\mathcal{H}=\gamma_S\vec{S}\cdot\vec{H}_0+\gamma\vec{S}\cdot\vec{N}. \tag{A-1}$$

The transition probability from a state $|N,M_N;\ S,M_S=\frac{1}{2}\rangle$ to a state $|N,M_N+1;S,M_S=-\frac{1}{2}\rangle$ after a time interval T is given by

$$W_{(\frac{1}{2}\to-\frac{1}{2})}=|\langle N,M_N+1;S,\ M_S=-\tfrac{1}{2}|e^{-i\mathcal{H}T/\hbar}|N,M_N;S,\ M_S=\tfrac{1}{2}\rangle|^2\ . \tag{A-2}$$

Let us denote by $\psi_\pm(M_j)$ the two eigenstates of $\mathcal{H}$ corresponding to a given eigenvalue M_J of $J_z=N_z+S_z$ (J_z is a good quantum number). By solving the secular equation the eigenenergies $\hbar\omega_\pm$ corresponding to $\psi_\pm$ are computed to be

$$\hbar\omega_\pm=\tfrac{1}{2}(\gamma\pm\hbar\omega)\,, \tag{A-3}$$

with $$\hbar\omega=[(\gamma_SH_0)^2+(\gamma N)^2+2\gamma_SH_0\gamma(M_N+\tfrac{1}{2})]^{1/2}. \tag{A-4}$$

The expansion of $\psi_\pm(M_J)$ in terms of the states $|N,M_N;S,M_S\rangle$ reads

$$\psi_\pm(M_J)=C_\pm^{1/2}(M_J)|NM_N;S\tfrac{1}{2}\rangle+C_\pm^{-1/2}(M_J)|N\,M_N;S-\tfrac{1}{2}\rangle\ , \tag{A-5}$$

with $$C_+^{1/2}/C_+^{-1/2}=-C_-^{-1/2}/C_-^{1/2}=\gamma[(N+M_N+1)(N-M_N)]^{1/2}/[\hbar\omega-\gamma_SH_0-\gamma(M_N+\tfrac{1}{2})]\ , \tag{A-6}$$

and $|C_\pm^{1/2}|^2+|C_\pm^{-1/2}|^2=1$.

Inserting in the expression for $W_{(1/2\to-1/2)}$ the eigenstates of $\mathcal{H}$ one obtains, using the orthogonality properties of the C's

$$W_{(1/2,-1/2)}=4|C_+^{1/2}C_+^{-1/2}\sin\tfrac{1}{2}\omega T|^2. \tag{A-7}$$

The expression has to be averaged over T and the intial values of N and M_N. Let us perform first the average over T. The relaxation rate reads

$$T_S^{-1}=4T_f^{-1}\langle|C_+^{1/2}C_+^{-1/2}|^2\omega^2\tau^2/(1+\omega^2\tau^2)\rangle_{\text{av }N,M_N}\ . \tag{A-8}$$

When the average is performed the largest contribution comes from values of N of the order of $\overline{N}=38$. If in the expressions for $C_\pm^{1/2}$ and ω terms of the order of $1/N$ are dropped, the error in T_S^{-1} will be of the order of $1/\overline{N}$:

$$\delta T_S/T_S=-2[\delta C_+^{1/2}/C_+^{1/2}+\delta C_+^{-1/2}/C_+^{-1/2}+(\delta\omega/\omega)\omega^2\tau^2/(1+\omega^2\tau^2)]\ . \tag{A-9}$$

Let us define $\cos\theta=M_N/N$. Neglecting terms of the order of $1/N$, ω can be rewritten as

$$\hbar\omega\approx[(\gamma_SH_0)^2+(\gamma N)^2+2\gamma_SH_0\gamma N\cos\theta]^{1/2}=|\gamma_S\vec{H}_0+\gamma\vec{N}|, \tag{A-10}$$

where $\vec{N}$ is a classical vector of length N such that $\vec{N}\cdot\vec{H}_0=NH_0\cos\theta$. Similarly

$$C_+^{1/2}/C_-^{1/2}\approx\gamma\sin\theta/(\hbar\omega-\gamma_SH_0-\gamma N\cos\theta)=\sin\alpha/(1-\cos\alpha)\,, \tag{A-11}$$

where α is the angle between $\gamma_S\vec{H}_0+\gamma\vec{N}$ and $\gamma_S\vec{H}_0$ (see Fig. 8). One finds immediately

$$2|C_+^{1/2}C_+^{-1/2}|=|\sin\alpha|. \tag{A-12}$$

The relaxation rate T_S^{-1} can be written finally as

$$T_S^{-1} = 2T_f^{-1}\langle \sin^2\alpha \sin^2\tfrac{1}{2}\omega T\rangle_{\text{av } N, M_N, T} \; . \tag{A-13}$$

This result is identical to the one given by the approximate treatment of Sec. V [see Eq. (66)] if the discrete average over N and M_N is replaced by an integral.

APPENDIX B

In this Appendix we are going to discuss the role of the two-body resonant collisions in the relaxation mechanism induced by "sticking" collisions. We have shown in Sec. III that the production and destruction of metastable states of intrinsic lifetime of the order of the time of flight or shorter is the result of two competing processes: (a) three-body collisions and (b) two-body resonant collisions.

In the absence of the external magnetic field, the relaxation rate induced by "sticking" collisions can be written as

$$\begin{aligned} T_S^{-1}(H_0=0) &= A(P) \\ &= \tfrac{2}{3}N_{\mathrm{Kr}} \sum_{v,N} \frac{\mathcal{P}(v,N)\omega_1^{2}(v,N)\tau^{t}(v,N)}{1+[\omega_1(v,N)\tau^{t}(v,N)]^2} \; . \end{aligned} \tag{B-1}$$

Here we have exhibited the explicit dependence of the total lifetime of the molecule $\tau^t(v,N)$ on the molecular state v,N. In Sec. V we have approximated $[\tau^t(v,N)]^{-1}$ by

$$[\tau^t(v,N)]^{-1} = \tau^{-1} = N_{\mathrm{Kr}}\mathcal{V}^{-1}\bar{\sigma}\bar{V}_{Mr} , \tag{B-2}$$

where $\bar{\sigma}$ is the average break-up cross section.

For metastable states we have simply to add the spontaneous decay rate

$$\begin{aligned} [\tau^t(v,N)]^{-1} &= N_{\mathrm{Kr}}\mathcal{V}^{-1}\sigma(v,N)\bar{V}_{Mr} + D(v,N)\tau_0^{-1} \\ &= [\tau^c(v,N)]^{-1} + D(v,N)\tau_0^{-1} , \end{aligned} \tag{B-3}$$

where τ_0 is the classical period and $D(v,N)$ the barrier-penetration coefficient (Sec. III, part F). No precise evaluation of $D(v,N)$ is possible; only upper and lower bounds have been derived:

$$e^{2\pi q a_v} < D(v,N) < e^{2\pi(q+1)a_v} \; , \tag{B-4}$$

where $q = N_{\max}(v) - N$ and a_v is a numerical coefficient tabulated in Table II. We have also kept the dependence on the molecular state of the break-up cross section $\sigma(v,N)$, since the energy transfer ΔE necessary to dissociate these states is much lower than the average value Δ. The break-up cross sections have been reevaluated using a straight-line approximation for the trajectory, and were found to be larger than the calculated value of $\bar{\sigma}$ roughly by a factor 2 with a slow variation with ΔE, i.e., $\sigma(v,N) \propto (\Delta E)^{1/6}$.

The role of two-body resonant collisions is illustrated by the value of the difference

$$\Delta A(P) = A_{ab}(P) - A_a(P) , \tag{B-5}$$

where $A_{ab}(P)$ and $A_a(P)$ are given by expression (B-1) by making the substitutions

$$[\tau^t(v,N)]^{-1} = \tau^c(v,N)^{-1} + D(v,N)\tau_0^{-1} ,$$

and $[\tau^t(v,N)]^{-1} = [\tau^c(v,N)]^{-1}$,

respectively. An upper bound of ΔA has been computed in the two extreme regions of low and high pressures, using (B-1), (B-3), (B-4), and then compared to the experimental values of $A(P)$ at the same pressures. The results are the following:

$P = 0.2$ Torr, $|\Delta A|/A < 0.12$
$P = 10$ Torr, $|\Delta A|/A < 0.16$.

This evaluation has been made by assuming that the strength of the spin-orbit interaction $\hbar\omega_1$ in the (v,N) level is

$$\hbar\omega_1(v,N) = \bar{\gamma}N \; , \tag{B-6}$$

where $\bar{\gamma}$ is taken from the analysis of the experimental data. Actually for the metastable states with high values of N lying near the top of the centrifugal barrier the value of

$$\langle\gamma(r)\rangle = \int |y_{vN}(r)|^2\gamma(r)dr ,$$

is certainly lower than $\bar{\gamma}$, since the centrifugal forces have a tendency to pull apart the two atoms of the molecule. Each term in the sum (B-1) being an increasing function of $\omega_1(v,N)$, we are overestimating $|\Delta A|$ by using (B-6).

The sign of $\Delta A/A$ is found positive at 0.2 Torr and negative at 10 Torr. This might be expected: an increase of the rate of formation (and destruction) of metastable states has a positive effect on the relaxation rate at low pressures when "sticking" collisions are "strong" ($T_S^{-1} \propto T_f^{-1}$), and a negative effect at high pressures when the motional narrowing condition applies ($T_S^{-1} \propto \tau^2 T_f^{-1}$).

Finally, over the entire range of pressures explored, the value 0.16 can be considered as an overestimated upper bound of $|\Delta A|/A$, and it is safe to conclude that resonant two-body collisions are of no practical importance. However, if experiments could be performed at lower pressure this would no longer be true: resonant two-body collisions would manifest themselves by inducing a relaxation rate proportional to P, instead of P^2.

---

[*] Associés au Centre National de la Recherche Scientifique, Paris, France.

[1] M. Aymar, M. A. Bouchiat, J. Brossel, Phys. Letters, 24A, 753 (1967); M. A. Bouchiat, J. Brossel, and L. Pottier, Phys. Rev. Letters 19, 817 (1967); and M. A. Bouchiat, J. Brossel, and L. Pottier, to be published.

[2] Electromagnetic forces between charged particles with spins are either velocity independent or linear in velocity in the nonrelativistic approximation.

[3] R. B. Bernstein and J. T. Muckerman, Theoretical Chemistry Institute, University of Wisconsin, Report No. 200, 1967 (unpublished); F. Von Busch, H. J. Strunck, C. Schlier, Z. Physik 199, 518 (1967).

[4] A. Dalgarno, T. N. L. Patterson, W. B. Somerville, Proc. Roy. Soc. (London), 259A, 100 (1960).

[5] R. M. Herman, Phys. Rev. 136, A1576 (1964). It was first proposed by Bernheim [J. Chem. Phys. 36, 135 (1962)] that the spin-orbit interaction is responsible for the disorientation of alkali atoms caused by collisions with a rare gas.

[6] M. A. Bouchiat, J. Phys. 24, 379 (1963).

[7] M. A. Bouchiat and L. Pottier, to be published.

[8] This condition is fully satisfied for the relaxation induced by "sudden" two-body collisions with a typical collision time of a few 10^{-12} sec. It will appear later on that the relaxation rates measured at 200 G, which are given in Table I, indeed correspond to such collisions.

[9] F. J. Adrian, Phys. Rev. 138, A403 (1965).

[10] H. Harrison and R. B. Bernstein, J. Chem. Phys. 38, 2135 (1963); and 47, 1884 (1967).

[11] The plots of the W. K. B. vibrational levels $E(v, N)$ versus $(N+1/2)^2$ actually present a slight downward curvature (not represented on Fig. 3) in the vicinity of the dissociation limit. This effect has been taken into account in the computation of $\mathcal{K}$.

[12] We have used the correspondence between b_0 and χ_0 computed for a 12-6 Lennard-Jones potential in the case of a relative energy equal to $E_i/2 = \frac{9}{8}\beta^{-1} = 2.8\epsilon$. Numerical data were found in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons Inc., New York, 1954), Table I R.

[13] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press, Oxford, 1958), p. 178.

[14] All pressures are supposed to be measured at 300° K.

[15] In a typical case when $\tau^e(v, N) = 10^{-8}$ sec, $E(v, N) = 0.3\epsilon$, and $N = 70$, one gets $\sigma(v, N) = 1.2\ 10^{-21}$ cm^2 and $[T_f^e(v, N)]^{-1} = 1.5$ sec^{-1} at $P = 1$ Torr.

[16] A. Abragam, Principles of Nuclear Magnetism (Oxford University Press, New York, 1961), Chap. 8.

[17] A new type of interatomic potential, which is a continuous modification of the Lennard-Jones 12-6 potential, has been recently suggested by Düren, Raabe, and Schlier [R. Düren, G. P. Raabe, C. Schlier, Z. Physik, 214, 410 (1968)]. They find that all experimental data available for the alkali-rare-gas systems Li-Kr, Na-Ar, Na-Xe, K-Ar and K-Kr can be fitted with one and the same set of values of the shape parameters involved. Extending this result to the Rb-Kr pair, we have computed the W. K. B. energies in this new potential and thence deduced the corresponding value of $\mathcal{K}$. We thus obtain $\mathcal{K} = 1.72 \times 10^{-22}$ cm^3/molecule.