Spin relaxation of atoms in molecular buffer gases

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LETTERS TO THE EDITOR

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possibility of an involvement of excited species other
than free atoms should not be overlooked although it
is unlikely that definitive conclusions will be possible
before considerable further experimental information
becomes available.

(1963).
(1964).
(1964).
6 K. F. Preston and R. J. Cvetanović (to be published).

Spin Relaxation of Atoms in Molecular Buffer Gases

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(Received 9 March 1965)

IN his discussion of the magnetic relaxation of
optically pumped rubidium in a buffer gas contain-
ing molecules with large electric-dipole moments,
McNeal\(^1\) develops a theory in which a static electric
field couples the two states \(S_\uparrow(1/2)\) in the limit
of zero magnetic field. This is forbidden by Kramers'
theorem (time-reversal invariance).\(^2,3\) The error
arises from the use of stationary perturbation theory in
the computation of a nonadiabatic effect.

Let an atom in the state \(m=\frac{1}{2}\) be exposed to a unifor-
magnetic field \(H\) oriented along the \(z\) axis, be
exposed to a uniform electric field \(E\) (not parallel to the
coordinate axes) for a period of time \(t\), where \(g_F\) is the
electron g factor and \(\mu_0\) is the Bohr
magneton. If we treat the electric field classically and
ignore the magnetic field arising from the time rate
of change of the electric field, then the probability
that a transition occurs between the state \(m\) and
the state \(k=\frac{3}{2}\) is given in second-order

time-dependent perturbation theory by

\[
P_{mk}(t) \sim \frac{2}{\hbar^2 \sum_{J_i}} \sum_{l=0}^{\infty} \frac{\langle i | 3l' \mid i \rangle \langle i | 3l' \mid m \rangle}{(E_m - E_i)}
\]

where \(3l'\) is the electric-dipole interaction defined by
McNeal, and the summation is over the excited \(p\)
states of the atom, which belong to the energy
eigenvalues \(E_i\). The sum which appears in this expression
is \(E_m - E_i\), \(C_k^{(2)} = g_F \mu_0 H \alpha_k^{(0)}\),
where \(C_k^{(2)}\) is the stationary-perturbation-theory coefficient
evaluated by McNeal. Since \(C_k^{(2)}\) is independent of \(H\), \(P_{mk} \rightarrow 0\) as
\(H \rightarrow 0\), as required by Kramers' theorem.

McNeal discusses the transition probability in terms of
an "effective magnetic field," that is, the magnetic
field which, when applied in the \(x\) direction for a time \(t,
\) yields the same transition probability \(P_{mk}\). This field
is \(2 \mid C_k^{(2)} \mid H\), which is smaller than \(H\). For a collision

between rubidium and a molecule of dipole moment
1.5 D at \(H=0.6\) G, \(P_{mk}\) is about \(10^{-2}\), so the electric-
field mechanism does not explain the experimental
results.

The author wishes to thank J. H. Van Vleck for
discussions of this problem.

\(^*\) Junior Fellow, Harvard Society of Fellows.
\(^2\) H. A. Kramers, Proc. Roy. Acad. Amsterdam 33, 959 (1930);
see L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addi-
son-Wesley Publishing Company, Inc., Reading, Massachusetts,

Spin transitions due to oscillating electric fields are discussed
in the theory of spin–lattice relaxation of paramagnetic salts. See
R. de L. Kronig, Physica 6, 33 (1939); J. H. Van Vleck, Phys.

Spin Relaxation of Rubidium in Molecular Buffer Gases

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(Received 9 April 1965)

IN the preceding comment\(^1\) Berg asserts that a
previous calculation\(^2\) of the spin-relaxation cross
section of optically oriented rubidium atoms in a buffer
gas containing molecules with large electric-dipole
moments is in error because of the use of stationary
perturbation theory in the calculation of a nonadiabatic
effect. Time-dependent perturbation theory was used,
however, in the previous calculation, although in a less
direct way than in Berg's Eq. (1). The error in the
previous calculation is in Eq. (24) of Ref. 2, which
should be written

\[
|H_1| |H| |C_k^{(2)}| \leq \frac{2}{\hbar^2 \sum_{J_i}} \sum_{l=0}^{\infty} \frac{\langle i | 3l' \mid i \rangle \langle i | 3l' \mid m \rangle}{(E_m - E_i)}
\]

where \(|H_1|\) is the magnitude of the effective magnetic
field and \(|H|\) is the magnitude of the applied Zeeman
field in the experiment. The calculation in Ref. 2 is
then essentially identical to Berg's. Both calculations
yield zero cross section in zero magnetic field in agree-
ment with Kramer's theorem. The author is indebted
to Berg for pointing out the discrepancy between his
calculation and the author's.

A correct treatment of the polar molecule-oriented
rubidium collision is not possible, therefore, when the
collision is simply represented by a time-dependent
electric field. The collision complex must be treated
on a molecular basis, and the effective Hamiltonian leading
to a spin reorientation must be derived explicitly.
Among the magnetic interactions arising during the
collisions, Bernheim\(^3\) has proposed an intramolecular
spin–rotation interaction to account for the relaxation
in rare-gas collisions. Herman\(^4\) has done detailed calcu-
lations for this interaction, and the results agree well
with experimental rare-gas cross sections. His calcu-
lation can be extended to polar buffer gases by includ-
ing the induction term in the intermolecular potential, but
the resulting cross section is too small to account for the observed result.

Large disorientation cross sections (in the range $10^{-17}$–$10^{-20}$ cm$^2$) have been observed for ammonia, dimethyl ether, and benzene. In a gas containing the latter molecule, a large, negative pressure shift of the $(F = 2, M_F = 0) \rightarrow (F = 1, M_F = 0)$ hyperfine transition frequency of the $^{87}$Rb ground state has been observed and attributed to a partial and transient electron transfer from rubidium to the benzene molecule during the collision. If such an electron transfer occurs also for the two polar molecules, then the large disorientation cross sections might result from interactions of the electron during association with the buffer-gas molecule rather than from intermolecular spin–rotation coupling.


On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids—Comment on a Paper by Adam and Gibbs

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(Received 20 May 1965)

An equation has been derived by Adam and Gibbs\(^1\) for the temperature dependence of the transition probability determining relaxation or flow of the form $W(T) = A \exp(-C/T S_e)$, $A$ being a temperature-insensitive frequency factor, $C$ dimensionally an energy, and $S_e$ the excess configurational entropy of the liquid, a quantity whose changes with $T$ or $P$ are experimentally measurable\(^2\) and whose magnitude is asserted, in a thermodynamic theory of the glass transition,\(^3\) to vanish at a temperature $T_e$, lying somewhat below the experimental $T_p$. They have further shown that this relation leads to an equation similar in form to the WLF equation\(^4\) and experimentally indistinguishable from it, and that the calorimetrically determined $S_e$ agrees with the value derived from the temperature dependence of relaxation processes. The ratio $T_e/T_p$ appears to have a nearly universal value of 1.30.

It is the purpose of this comment to point out three further types of experiments for which the Adam–Gibbs equation gives either quantitative or qualitative agreement, which the free-volume theory notoriously fails to do: these are pressure dependence, volume relaxation below $T_e$, and plasticity.

O’Reilly\(^4\) has shown that the pressure coefficient of $T_e$ is approximately equal to $T V \Delta \alpha / \Delta C_p$, but only about half as great as $\Delta \beta / \Delta \alpha$ (see Ref. 2 or 5 for definitions). Additional evidence that this is an almost general situation was reviewed by the author.\(^6\) In the author’s earlier paper\(^6\) it was shown that the experimental situation $dT_e/dP = TV \Delta \alpha / \Delta C_p < \Delta \beta / \Delta \alpha$ implies that free volume cannot determine relaxation times, but either configurational entropy or enthalpy could. It seemed then that the approximate universality of $\Delta C_p$ as contrasted with the variability of $\Delta C_p / T_e$ implied the WLF equation could not be deduced from an entropy criterion, but could from an enthalpy one. It appears however that, if relaxation times are a function of the product $T S_e$, the WLF equation can be derived; it is further true that a nearly correct pressure dependence can be deduced: on the assumption of a negligible activation volume (see, however, below) and a constant $\Delta C_p$ down to $T_2$ the following results:

$$
\frac{dT_e}{dP} = T_e V \Delta \alpha / \Delta C_p.
$$

The difference between this and O’Reilly’s equation applied near $T_e$ is about 30%; it is not clear that the experimental data are precise enough to make the distinction, or for that matter whether quantitative agreement of a greater degree than this should indeed be demanded of the theory.

The Adam–Gibbs formula contains both an explicit dependence on temperature and an implicit one through $S_e$, the latter reflecting the changing structure of the liquid. It has been pointed out that experimental studies of volume flow in the glass transition region, where the structure can be temporarily frozen in while temperature is changed, permit a separation of a direct from an implicit effect of temperature\(^6\); a role for both is found; the relative importance of each depends on the particular substance; structure dominates in polyvinyl acetate,\(^6\) but the two being of about equal importance in borosilicate glass\(^6\) and zinc chloride.\(^6\) The ratio of the structural to the direct effect can be shown from the Adam–Gibbs equation to be $\Delta C_p / S_e$ whose universal value is about 3. This agrees well with the measurements on polyvinyl acetate both in shear\(^6\) and volume.\(^7\) There are no experimental data on $\Delta C_p$ or $S_e$ in either borosilicate glass or zinc chloride. In any event the qualitative correctness of the Adam–Gibbs equation is to be noted, in contrast to the need in free-volume theories to introduce quite ad hoc a temperature dependence of free volume below $T_e$.

The Adam–Gibbs equation can be viewed as a reversion to the idea of viscosity as a thermally activated process,\(^9\) but with the rapidly changing activation energy near $T_e$ explained by the changing structure. Their derivation proceeds through the calculation of the free energy of an activated state, which therefore contains a volume of activation $V^*$ as well as an energy of activation: $W(T)$ is thus more generally written as

$$W(T) = A \exp\left[-(C + DP)/TS_e\right].$$