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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.

¹ H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.* **39**, 1902 (1963).

² H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.* **40**, 582 (1964).

³ H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.* **41**, 3703 (1964).

⁴ P. Warneck, *Discussions Faraday Soc.* **37**, 57 (1964).

⁵ P. Warneck, *J. Chem. Phys.* **43**, 1849 (1965).

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

Spin Relaxation of Atoms in Molecular Buffer Gases

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IN his discussion of the magnetic relaxation of optically pumped rubidium in a buffer gas containing molecules with large electric-dipole moments, McNeal¹ develops a theory in which a static electric field couples the two states $^2S_{\frac{1}{2}}(M_J = \pm \frac{1}{2})$ 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 $m = ^2S_{\frac{1}{2}}(M_J = \frac{1}{2})$, which is at rest in a magnetic field H oriented along the z axis, be exposed to a uniform electric field $\mathbf{E}$ (not parallel to the coordinate axes) for a period of time $\tau \ll (g_J \mu_0 H / \hbar)^{-1}$, where g_J is the electron g factor and μ_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 $k = ^2S_{\frac{1}{2}}(M_J = -\frac{1}{2})$ is given in second-order time-dependent perturbation theory by

$$P_{mk} \sim \frac{\tau^2}{\hbar^2} \left| \sum_{i \neq m} \frac{\langle k | \mathcal{H}' | i \rangle \langle i | \mathcal{H}' | m \rangle}{(E_m - E_i)} \right|^2, \quad (1)$$

where $\mathcal{H}'$ 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 $(E_m - E_k) C_k^{(2)} = g_J \mu_0 H C_k^{(2)}$, 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 τ , yields the same transition probability P_{mk} . This field is $2 | C_k^{(2)} | H$, 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^{-12} , 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.

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¹ R. J. McNeal, *J. Chem. Phys.* **40**, 1089 (1964).

² H. A. Kramers, *Proc. Roy. Acad. Amsterdam* **33**, 959 (1930); see L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 202.

³ 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. Rev.* **57**, 426 (1940); and R. Orbach, *Proc. Phys. Soc. (London)* **77**, 821 (1961); *Proc. Roy. Soc. (London)* **A264**, 458, 485 (1961).

Spin Relaxation of Rubidium in Molecular Buffer Gases

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IN the preceeding comment¹ Berg asserts that a previous calculation² 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

$$| \mathbf{H}_1 |^2 \alpha | \mathbf{H} |^2 | C_k^{(2)} |^2,$$

where $| \mathbf{H}_1 |$ is the magnitude of the effective magnetic field and $| \mathbf{H} |$ 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 agreement with Kramers' 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, Bernheim³ has proposed an intermolecular spin-rotation interaction to account for the relaxation in rare-gas collisions. Herman⁴ has done detailed calculations for this interaction, and the results agree well with experimental rare-gas cross sections. His calculation can be extended to polar buffer gases by including 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} cm²) 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 ⁸⁷Rb ground state has been observed and attributed to a partial and transient electron transfer from rubidium to the benzene molecule during the collision.⁵ 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.

¹ H. C. Berg, J. Chem. Phys. **43**, 1851 (1965).

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

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AN equation has been derived by Adam and Gibbs¹ for the temperature dependence of the transition probability determining relaxation or flow of the form $W(T) = A \exp(-C/TS_e)$, 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 measurable² and whose magnitude is asserted, in a thermodynamic theory of the glass transition,³ to vanish at a temperature T_2 , lying somewhat below the experimental T_g . They have further shown that this relation leads to an equation similar in form to the WLF equation⁴ 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_g/T_2 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 notably fails to do: these are pressure dependence, volume relaxation below T_g , and plasticity.

O'Reilly⁵ has shown that the pressure coefficient of T_g is approximately equal to $TV\Delta\alpha/\Delta C_P$, 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.² In the author's earlier paper² it was shown that the experimental situation $dT_g/dP = TV\Delta\alpha/\Delta C_P < \Delta\beta/\Delta\alpha$ implies that free volume cannot determine relaxation times, but either configurational entropy or enthalpy could. It seemed then that the approximate universality of ΔC_P as contrasted with the variability of $\Delta C_P/T_g$ 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 TS_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 ΔC_P down to T_2 the following results:

$$dT_g/dP = T_2 V \Delta\alpha / \Delta C_P.$$

The difference between this and O'Reilly's equation applied near T_g 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 temperature⁶; a role for both is found; the relative importance of each depends on the particular substance; structure dominates in polyvinyl acetate,⁷ but the two being of about equal importance in borosilicate glass⁸ and zinc chloride.⁸ 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 shear⁹ and volume.⁷ There are no experimental data on ΔC_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_g .

The Adam-Gibbs equation can be viewed as a reversion to the idea of viscosity as a thermally activated process,¹⁰ but with the rapidly changing activation energy near T_g 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

$$\frac{A}{\exp[-(C+DP)/TS_e]},$$