

when setting $[^{36}\text{O}_2(a^1\Delta_g)] = 0$ at $t=0$, $k_1 = k_{-1}$, and assuming that mixing is instantaneous. Wall deactivation of $\text{O}_2(a^1\Delta_g)$ cancels out in this expression. For the lowest concentrations used,

$$\begin{aligned} [^{32}\text{O}_2(X^3\Sigma_g^-)] &= [^{36}\text{O}_2(X^3\Sigma_g^-)] \\ &= 1.1 \times 10^{-8} \text{ mol liter}^{-1}, \end{aligned}$$

and the minimum contact time of 4×10^{-3} sec, taking $Q > 0.5$, yields the lower limit, $k_1 > 1 \times 10^{10}$ liter $\text{mol}^{-1} \cdot \text{sec}^{-1}$. This corresponds to energy transfer at least once in every 10 hard sphere collisions. This very rapid energy transfer from $\text{O}_2(a^1\Delta_g)$ to $\text{O}_2(X^3\Sigma_g^-)$, essentially equal to that found¹ for $\text{NO}(A^2\Sigma)$ to $\text{NO}(X^2\Pi)$, is in disagreement with the prediction of the Gordon-Chiu theory² and suggests that another mechanism is required.

Experiments involving longer contact times failed to show any significant increase in the ratio

$$[^{34}\text{O}_2(a^1\Delta_g)] / [^{36}\text{O}_2(a^1\Delta_g)]$$

over the original isotopic purity of the $^{36}\text{O}_2$. Combining the lower limit for $k_1 = 1 \times 10^{10}$ liter $\text{mol}^{-1} \cdot \text{sec}^{-1}$, and the fact that a 50% conversion of $^{36}\text{O}_2(a^1\Delta_g)$ to $^{34}\text{O}_2(a^1\Delta_g)$ would have been readily detected, it was concluded that no significant isotopic scrambling occurred even after 10^8 energy transfers. Hence Reaction (1) involves energy transfer only, with little or no atomic rearrangement.

Since the rate of energy transfer in O_2 is comparable

to the collision rate, some other mechanism, not involving the very small transition moment, is required. It is possible that the optical selection rules are relaxed during the collision of two oxygen molecules. However, the magnitude of the pressure-induced absorption observed⁴ for $\text{O}_2(a^1\Delta_g \leftarrow X^3\Sigma_g^-)$ suggests this relaxation only increases the transition moment by about a factor of 10^3 . Electron exchange provides an alternative mechanism for energy transfer. Estimates of the exchange integral for a $\text{O}_2\text{-O}_2$ collision complex show that such a mechanism is feasible. If electron exchange is responsible for the rapid electronic energy transfer observed in O_2 , then it may also account for the rapid energy transfer observed in NO .

Support from the U. S. Air Force Office of Scientific Research (AFOSR-70-1872) and the Public Health Service (USPHS-APO-1254-01) is gratefully acknowledged.

¹ L. A. Melton and W. Klemperer, *J. Chem. Phys.* **55**, 1468 (1971).

² R. G. Gordon and Y. N. Chiu, *J. Chem. Phys.* **55**, 1469 (1971).

³ H. P. Broida and T. Carrington, *J. Chem. Phys.* **38**, 136 (1963).

⁴ R. M. Badger, A. C. Wright, and R. F. Whitlock, *J. Chem. Phys.* **43**, 4345 (1965).

⁵ J. T. Herron and F. S. Klein, *J. Chem. Phys.* **40**, 2731 (1964).

⁶ K. Furukawa, and E. A. Ogryzlo, *Chem. Phys. Letters* **12**, 370 (1971).

⁷ H. D. Sharma, R. E. Jervis, and K. Y. Wong, *J. Phys. Chem.* **74**, 923 (1970).

⁸ I. T. N. Jones and K. D. Bayes, *Chem. Phys. Letters* **11**, 163 (1971).

Calculation of Magnitudes of Chemically Induced Dynamic Electron Polarizations*

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(Received 21 April 1972)

Recently, there have been several very interesting observations of anomalous ESR spectra arising from nonequilibrium populations of the spin levels for some short-lived free radicals generated in liquids by irradiation or chemical reaction.¹ There have been several initial attempts to explain such observations^{2,1f} (in a manner analogous to those offered for CIDNP) in terms of the combined effects of (1) an exchange interaction between a radical pair formed from a dissociating molecule and (2) differences in the Larmor frequencies between the two radicals in the pair by virtue of different g values or different hyperfine interactions with their respective magnetic nuclei. Perhaps the most satisfying analysis to date is that

given by Adrian,^{2c} who considered the situation where the radical pair may separate by diffusion, but then suffers a new encounter. This has the particular advantage of allowing the polarization process to be broken up into two steps of differing time duration. Adrian's approach, while highly instructive, is still incomplete in that he is not able to calculate average quantities involving averaging of the effects of the exchange interaction over the range of possible radical-pair trajectories; he could only guess at order-of-magnitude values.

It is possible, however, to perform a rigorous analysis of the electron-spin polarization generated by the radical-pair mechanism by means of the stochastic-

TABLE I. Limiting CIDEP polarizations $P_1 \times 10^3$ ^a (P_1 values are to the right of values of parameters varied).

Parameter varied						
J_0 (sec ⁻¹)	10 ⁶ / 0.038	10 ⁸ / 3.84	10 ¹⁰ / 212	10 ¹² / 7.71	10 ¹³ / 5.38	10 ¹⁵ / 4.78
D (cm ² /sec)		10 ⁻³ / 0.544	10 ⁻⁴ / 0.885	10 ⁻⁵ / 5.38	10 ⁻⁶ / 14.5	10 ⁻⁷ / 9.27
D^b (cm ² /sec)		10 ⁻³ / 11.8	10 ⁻⁴ / 13.1	10 ⁻⁵ / 15.6	10 ⁻⁶ / 7.78	10 ⁻⁷ / 8.01
$r_{EX}'^c$ (Å)		8 ^o / 24.8	4 / 7.68	2 / 5.38	1 / 2.56	0.2 / 0.539
Δr^d (Å)		$\frac{1}{2}$ / 3.58	$\frac{1}{2}$ / 5.38	1 / 12.1	2 / 0.930	

^a The "realistic" values utilized to calculate P_1 are $r_1 = 4$ Å, $\Delta r = \frac{1}{2}$ Å, $J_0 = 10^{13}$ sec⁻¹, $r_{EX}' = 2$ Å, $D = 10^{-5}$ cm²/sec, $\Delta H_{1,2} = 1 \times 10^8$ sec⁻¹ (methyl proton splitting) except as these parameters are varied.

^b Here $\Delta H_{1,2} = 2.2 \times 10^9$ sec⁻¹ (H atom splitting).

^c Here r_{EX}' is given as the number of angstroms beyond r_1 for $J(r)$ to drop to 10^{-5} of its contact value, J_0 .

^d This is the radial jump length used for 4–10 Å separations. Larger jump lengths are used for > 10 Å where $J(r)$ is negligible.

^e $\Delta r = 1$ Å utilized.

Liouville method,³ wherein $\rho(\mathbf{r}, t)$, the spin-density matrix equation of motion includes simultaneously the effects of spin-dependent parameters and also the effects of translational diffusion, that is, $\partial/\partial t \rho(\mathbf{r}, t) = -i[\mathcal{H}(\mathbf{r}), \rho(\mathbf{r}, t)] + D\nabla^2 \rho(\mathbf{r}, t)$, where $\mathcal{H}(\mathbf{r})$ is the Hamiltonian for the radical-pair dependent on inter-radical vector \mathbf{r} via the exchange interaction $J(\mathbf{r})$, and $D\nabla^2$ is the translational-diffusion operator with relative diffusion coefficient D . By solving this equation, one automatically includes the appropriate ensemble average over *all* the trajectories for the diffusive motion and how they modulate $J(\mathbf{r})$, etc. Thus, one simultaneously includes the effects of radical-radical re-encounters^{2c} and of any possible adiabatic effects,^{1f, 2b} any possible polarization effects during a single encounter,^{2a} and any other submodel one may wish to propose.

We have obtained computer solutions for isotropic $J(\mathbf{r}) = J(r)$, with the initial condition taken as two radicals in contact and either pure singlet (S_0) or pure triplet (T_0) (or any mixture of the two). One can then readily show that the electron-spin polarization of one radical of the pair is given by (neglecting $T_{\pm 1}$ states and any recombination reactions for simplicity^{2c})

$$P_1(t) = 2 \operatorname{Re} \int_0^\infty r^2 \rho(r, t)_{S,T} dr$$

where $\rho(r, t)_{S,T}$ is the off-diagonal matrix element of ρ between the S_0 and T_0 states. One may utilize finite difference techniques, wherein (1) the continuous range in r becomes discrete segments and (2) r is constrained to some finite but large enough maximum value r_{\max} (i.e., a spherical box) such that this boundary (taken as an absorbing wall) has hardly any effect on the results.

We give, in Table I, typical results of the limiting polarization [$\lim_{t \rightarrow \infty} P_1(t)$] for a range of values of the relevant parameters. {It was assumed that $J(r) = J_0 \exp[-(r-r_1)/r_{EX}']$, where r_1 is the contact distance for the two radicals.} One finds that there are a wide

range of conditions for which P_1 is comparable to, or greater than, the Boltzmann factor of 1.4×10^{-8} for room temperature and 9 GHz Larmor frequency. In particular this is true for the "realistic" values of the parameters taken as the basis for the table. However, there are a number of trends which are discernible: (1) For $J_0 > 10^{12}$ sec⁻¹, P_1 becomes nearly independent of J_0 , while it first rises for $10^8 < J_0 < 10^{12}$ and then it drops off rapidly for small J_0 . (2) Large values of P_1 are obtained for reasonable values of $D = 10^{-5}$ cm²/sec and $\Delta H_{1,2} = 1 \times 10^8$ sec⁻¹, but it drops off markedly as the diffusion is greatly speeded up, while it tends to level off as the motion slows down. (3) Around $D = 10^{-5}$ cm²/sec, P_1 depends on $\Delta H_{1,2}$ (half the Larmor frequency difference between interacting radicals) in a manner that is slightly weaker than $\Delta H_{1,2}^{1/2}$, but the dependence on $\Delta H_{1,2}$ is markedly affected when a large change is made in the value of D . (4) P_1 is a sensitive function of r_{EX} , dropping off rapidly for small r_{EX} (which approaches the model of $J_0 = 0$ as soon as the radical separates). (5) The effects of r_{EX} on P depends also on the value of Δr , the mean jump distance (as well as $\Delta H_{1,2}$), and typical effects of Δr are also given. Note that the mean jump time τ is equal to $\Delta r^2/6D$. These trends taken together represent a more complex dependence of the relevant parameters than any of the simple models previously proposed although the roughly approximate $\Delta H_{1,2}^{1/2}$ dependence of P_1 (but only for D of the order of 10^{-5} cm²/sec) is in accord with Adrian's model^{2c} and the experimental results of Paul and Fischer.^{1c}

It should be noted that the signs of P (emissive or absorptive) we obtain are exactly those expected given the signs of J_0 and $\Delta H_{1,2}$.² While our results in Table I are given for radicals initially in contact and in a singlet state, a wide variety of initial states and reactive possibilities for the radicals may also be dealt with by this method.

The method is also applicable to CIDNP and for generalized models of Heisenberg spin exchange.

We wish to thank G. V. Bruno for his considerable aid with the computer programming.

* Supported in part by the National Science Foundation (Grant No. GP-13780) and the Material Science Center, Cornell University.

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¹ (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* **39**, 2147 (1963). (b) B. Smaller, J. R. Remko, and E. C. Avery, *ibid.* **48**, 5174 (1968). (c) H. Paul and H. Fischer, *Z. Naturforsch.* **25a**, 443 (1970). (d) P. W. Atkins, I. C. Buchanan, R. C. Gurd, K. A. McLaughlan, and A. F. Simpson, *Chem. Commun.* **9**, 513

(1970). (e) R. Livingston and H. Zeldes, *J. Chem. Phys.* **53**, 1406 (1970). (f) S. H. Glarum and J. H. Marshal, *ibid.* **52**, 5555 (1970).

² (a) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Letters* **4**, 195 (1969). (b) H. Fischer, *ibid.* **4**, 611 (1970). (c) F. J. Adrian, *J. Chem. Phys.* **54**, 3918 (1971). (d) P. W. Atkins, R. C. Gurd, K. A. McLaughlan, and A. F. Simpson, *Chem. Phys. Letters* **8**, 55 (1971). (e) F. J. Adrian, *ibid.* **10**, 70 (1971).

³ (a) R. Kubo, *Advan. Chem. Phys.* **16**, 101 (1969); *J. Phys. Soc. Japan, Suppl.* **26**, 1 (1969); (b) J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.* **75**, 3385 (1971); *J. Chem. Phys.* **55**, 5270 (1971); (c) J. H. Freed, in *ESR Relaxation in Liquids* edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 57, NUMBER 2

15 JULY 1972

Light Scattering from Ionic Liquids

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(Received 27 March 1972)

A number of mechanisms have been proposed to account for the inelastic light scattering that is observed for liquids as a continuum extending from ~ 10 cm^{-1} to ~ 300 cm^{-1} from the incident frequency. On the basis of a dipole-induced-dipole (DID) model the spectrum of liquid argon has been interpreted in terms of two-phonon Raman scattering.¹ Alternatively,² it has been proposed that in nonpolar liquids the scattering arises from isolated binary collisions (IBC model).

The purpose of this preliminary Communication is to propose that in ionic (and possibly also dipolar) liquids the predominant scattering is produced by different mechanisms, which occur in response to local charge fluctuations within the liquid. For spherical polarizable ions these fluctuations will result in charge-induced anisotropy (CIA). In the case of anisotropic ions, angular motions of the permanent polarizability anisotropy may also occur.³

The spectrum of liquid KCl at 1073°K (excited by 5145 Å light from an argon-ion laser) is shown in Fig. 1. The apparatus used for these experiments is described elsewhere.⁴ It is found that the spectrum has the familiar^{1,2} quasiexponential form centered on zero frequency. The intensity at 100 cm^{-1} is less than 10% of the ν_1 Raman peak height for carbon tetrachloride at 25°C using the same instrumental slitwidth of 2 cm^{-1} . A notable feature of the scattering is that it is highly polarized, in contrast to the scattering from liquid argon¹ and simple molecular liquids² which is essentially depolarized. This difference may be understood at least qualitatively by considering the spatial dependence of the relevant perturbing forces. For nonpolar liquids, Bucaro and Litovitz² assumed an r^{-9} dependence of the interaction force (r is the internuclear distance) which decreases rapidly with increasing distance and gives

some justification to the IBC model. In the CIA model, however, the polarizing force is proportional to r^{-2} so that many surrounding ions will be involved simultaneously. The ionic motions cannot be described in a simple manner but it is reasonable to expect not only deformation of the electronic polarizability but also significant fluctuations of its isotropic part, leading to an appreciable intensity of polarized scattering.

In order to test the appropriateness of the CIA model, a power spectrum corresponding to polarized scattering was computed numerically using the method

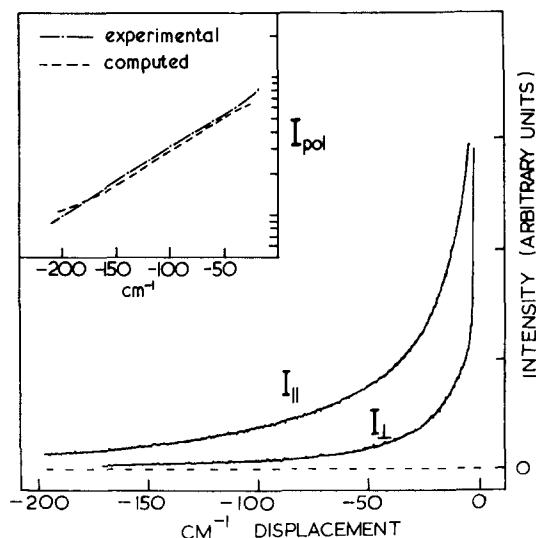


Fig. 1. Inelastic light scattering from liquid KCl at 1073°K. $I_{||}$ and I_{\perp} are, respectively, the observed scattering with electric vector parallel to and perpendicular to that of the incident light. The inset shows the experimental and computed trace scattering (I_{pol}) on a logarithmic intensity scale. $I_{pol}(\omega) = (I_{||}(\omega) - \frac{1}{2}I_{\perp}(\omega))$.