

¹⁹F dynamic nuclear polarization studies on the system CF₂Cl–CFCl₂/tertiary butyl phenoxy radical: Evidence for indirect chlorine participation in enhancing fluorine scalar rates

N. Chandrakumar and P. T. Narasimhan

Citation: *The Journal of Chemical Physics* **77**, 2697 (1982); doi: 10.1063/1.444102

View online: <http://dx.doi.org/10.1063/1.444102>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/77/5?ver=pdfcov>

Published by the [AIP Publishing](#)



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



production σ that is traditionally considered due to irreversible phenomena in the system. Therefore, we look for σ in the form $\sigma = \sum_{i\alpha} T^{-1} X_i^{(\alpha)} \circ \Lambda_i^{(\alpha)}$, where the $X_i^{(\alpha)}$ are determined from the consistency conditions, Eqs. (3.12a) in I, and T is to be identified with non-equilibrium temperature.

With the kinetic expression for $\Lambda_i^{(\alpha)}$ put into the formula for σ just given and comparing the latter with its statistical formula, we infer that f_i must be of the form $\log f_i = -\beta(H_i + H_i^{(1)} - \mu_i)$, where H_i is the kinetic energy of the particle in the frame of reference moving with the fluid velocity, $H_i^{(1)} = \sum_{\alpha} X_i^{(\alpha)} \circ h_i^{(\alpha)}$, $\beta = 1/k_B T$, and μ_i is the normalization factor.

Since $h_i^{(\alpha)}$ are functions of the velocity, the expansion in $h_i^{(\alpha)}$ for f_i must be such that the normalization integral of f_i is defined. In order to assure it, it is safe to put a convergence factor $\exp[-\epsilon q(u_i)]$ in the integral:

$$\exp(-\beta \mu_i) = \lim_{\epsilon \rightarrow 0} n_i^{-1} \langle \exp[-\epsilon q(u_i)] \exp[-\beta(H_i + H_i^{(1)})] \rangle, \quad (2)$$

where $q(u_i) = \text{Sup}_u |H_i^{(1)}|$. In practice, one does not have a complete set for the expansion for $H_i^{(1)}$. Therefore, when it is truncated, it must be done such that the integral is well defined or the convergence factor must be put in. This must be understood even if it is not explicitly stated.

The consistency conditions are tantamount to the statement that there exists a nonclassical contribution

to the entropy flux $\sum_{i\alpha} X_i^{(\alpha)} \circ \psi_i^{(\alpha)} / T$, in addition to the classical contribution $\sum_i (Q_i - \hat{\mu}_i J_i) / T$ (see I for the notations). It is a practical necessity to have a differential form for the entropy change in the Gibbs space in order to have a practicable theory of irreversible thermodynamics for systems removed far from equilibrium. The nonclassical term is essential for the existence of a differential form for the entropy density and its integrability conditions to be defined.

Since the extended Gibbs relation means that f_i can be expressed in terms of the entropy derivatives with respect to the Gibbs variables, s may be written as $s = \sum_a \partial_a (\partial s / \partial \partial_a)_{\xi}$, where ∂_a denotes a Gibbs variable and the subscript ξ means keeping the other Gibbs variables fixed in the differentiation. This shows that s is a first degree homogeneous function of the Gibbs variables in the moving frame of reference. This important result owes its emergence to the extended Gibbs relation directly and to the form of σ taken in terms of $\Lambda_i^{(\alpha)}$ and the consistency conditions indirectly. This relation can be useful for developing thermodynamic theory^{2(b)} for systems removed far from equilibrium.

¹B. C. Eu, J. Chem. Phys. 73, 2958 (1980); will be referred to as I.

²(a) B. C. Eu, J. Chem. Phys. 74, 2998 (1981); (b) 74, 6381 (1981).

¹⁹F dynamic nuclear polarization studies on the system CF₂Cl-CFCl₂/tritertiary butyl phenoxy radical: Evidence for indirect chlorine participation in enhancing fluorine scalar rates

N. Chandrakumar^{a)} and P. T. Narasimhan^{b)}

Department of Chemistry, Indian Institute of Technology, Kanpur-208 016, India
(Received 18 March 1981; accepted 21 September 1981)

The enhancement of scalar coupling at nuclei by the presence of chlorine in the same molecule is a well-known phenomenon in dynamic nuclear polarization (DNP) studies. The effect has been noted¹⁻³ in studies on ¹⁹F, ³¹P, and ¹³C. In general, however, the mechanism of chlorine participation has remained obscure. In particular, two classes of mechanisms are to be distinguished: the direct participation mechanism, with the chlorine acting as a spin messenger and the indirect participation mechanism, with the presence of chlorine affecting the electronic environment at the nucleus of interest and thus enhancing scalar rates. Bates, has reported¹ DNP studies on CFCl₃ and CFCl₂H at 75 G and finds an abnormal aliphatic fluorine scalar rate, to be attributed to the presence of chlorine. In our

laboratory, X-band studies on the system Freon-113 (CF₂Cl-CFCl₂)/TTBP (tri-*t*-butylphenoxy radical) had indicated⁴ a higher scalar rate at the -CFCl₂ fluorine. We have confirmed these findings on our field-frequency locked medium resolution X-band DNP spectrometer,^{5,6} with relative enhancements of the fluorines being $A_{F(-CF_2Cl)} \approx -1.4$ and $A_{F(-CFCl_2)} \approx -0.7$. The experiments were performed at $25 \pm 2^\circ\text{C}$. The solvent and radical precursor were obtained from K & K Laboratories, U.S.A. The radical was generated in the NMR sample tube itself by adding excess, freshly-prepared nickel peroxide to the solvent with dissolved precursor. The tri-*t*-butylphenol precursor was used after recrystallization from methanol. The DNP sample was freed of dissolved oxygen by bubbling oxygen-free nitrogen

TABLE I. Some parameters of electronic structure for the molecule $\text{CF}_2\text{Cl}-\text{CFCl}_2$ (Freon-113). p_1 and p'_1 are lone-pair p -orbitals. Experimental trend in scalar rates: $\text{F}(-\text{CFCl}_2) > \text{F}(-\text{CF}_2\text{Cl})$.

Nucleus	(sp_σ) -polarizability		Valence-shell electron density	Valence-shell orbital occupancies			
	EH	SCF/CNDO		s	p_σ	p_1	p'_1
$\text{F}(-\text{CF}_2\text{Cl})$	0.1555	0.0905	7.1734	1.8305	1.4040	1.9749	1.9640
$\text{F}(-\text{CFCl}_2)$	0.1663	0.0915	7.1519	1.8463	1.3555	1.9795	1.9706

gas. Radical concentration, as estimated from precursor concentration, was $\approx 5 \times 10^{-2}$ M.

Although we could not obtain the extrapolated U_∞ values⁷ owing to the very small effects observed at the low microwave power available to us, the differential trends are unmistakable. The differential effects are to be attributed to differences in the scalar interaction, the dipolar interaction not being sensitive to the chemical environment of nuclei.

In an effort to correlate the observed trends with the molecular electronic structure, we have adopted a closed-shell perturbation formalism along the lines of Dwek *et al.*⁸ Such an approach ought to be capable of describing our experimental situation, since the TTBP radical used in our studies is known to interact with the solvent molecules by exchange polarization, and not by specific chemical interaction.⁹ Treating the exchange interaction between the radical unpaired electron and the electrons of the solvent molecule as the perturbation⁸ and approximating the singlet-triplet excitation energies by molecular orbital (MO) level differences¹⁰ the spin density induced at nucleus M in the solvent molecule can be written as

$$\delta_M = -2 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \sum_{M', M'', b', b''} (\epsilon_i - \epsilon_j)^{-1} C_{i s, M} C_{j s, M} \times C_{i b', M'} C_{j b'', M''} \langle \phi_{s, M} | \delta_M(r) | \phi_{s, M} \rangle \times \langle \phi_{b', M'} \psi_R^0 | \frac{e^2}{r} | \psi_R^0 \phi_{b'', M''} \rangle \quad (1)$$

Subscripts M, M', and M'' refer to the atomic centers while i and j refer to the occupied and unoccupied MO's in the closed-shell solvent molecule. ϵ 's are MO energies. ϕ 's refer to the atomic orbitals (AO) in the solvent molecule while ψ_R^0 is the oxygen AO of the radical. $C_{i s, M}$ is the coefficient of the valence s orbital $\phi_{s, M}$ centered on M in the i th occupied MO. b' and b'' are the valence-shell AO's centered on M' and M'', respectively. $\delta_M(r)$ is the Dirac δ -function operator centered on nucleus M. Only one-center integrals of this operator are retained. We are interested here in the spin density on fluorine nucleus. Since the fluorine atoms lie at the periphery of the molecule we retain only terms with $M' = M''$ in Eq. (1). The valence-shell s orbital of fluorine is energetically and spatially deeply buried in comparison with p orbitals and consequently we retain in the summation over b' , b'' in Eq. (1) only the terms involving p orbitals. Note that in Eq. (1) now the coefficient of the s orbital of a fluorine atom appears along with the

coefficient of the p orbital on the same atom for a given MO. This p orbital is a p_σ orbital along the C-F bond direction. It is thus seen that the induced spin density is proportional to the (sp_σ) -parameter defined as

$$(sp_\sigma)_{MM} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{i s, M} C_{j s, M} C_{i p_\sigma, M} C_{j p_\sigma, M} \quad (2)$$

Noting the analogy with the polarizability parameter of Coulson and Longuet-Higgins¹¹ we refer to the quantity $(sp_\sigma)_{MM}$ as a (sp_σ) polarizability parameter.

We have calculated the relevant (sp_σ) polarizability parameter for the "Freon-113" molecule in the extended Hückel (EH) as well as the CNDO framework,¹⁰ using the "CNINDO" program,¹² modified suitably for our purposes. Input atom coordinates were obtained from electron diffraction data¹³ on the bond lengths and bond angles in this molecule. We summarize our results for this system in Table I. Also included in this table are the valence-shell electron densities and valence-shell orbital population analysis for the two representative inequivalent fluorine atoms. Clearly, the fluorine atom exhibiting the higher scalar rate is also associated with the higher value of the (sp_σ) -polarizability parameter. In addition, it also has the lower valence-shell electron density, arising essentially from the lower p_σ population. In this system at least, therefore, it does not appear necessary to invoke the direct participation of chlorine to understand the observed trend in scalar rates.

It is with great pleasure that the authors acknowledge: Dr. N. Sathyamurthy of the Department of Chemistry, I. I. T., Kanpur, for kindly providing us the relevant QCPE program tape; Mr. P. P. Thankachan, Dr. V. H. Subramanian, Mr. S. Shankar, and Miss A. Tripathi for helpful discussions.

^{a)} Present address: Chemical Laboratories, Central Leather Research Institute, Adyar, Madras-600 020, India.

^{b)} To whom all correspondence should be addressed.

¹R. D. Bates, Jr., *J. Chem. Phys.* **66**, 1759 (1977).

²W. Müller-Warmuth and R. Vilhjalmsson, *Z. Phys. Chem.* **93**, 283 (1974).

³W. Müller-Warmuth, R. Vilhjalmsson, P. A. M. Gerlof, J. Smidt, and J. Trommel, *Mol. Phys.* **31**, 1055 (1976).

⁴S. Aravamudhan, Ph.D. thesis, Indian Institute of Technology, 1974.

⁵N. Chandrakumar, Ph.D. thesis, Indian Institute of Technology, 1979.

⁶N. Chandrakumar and P. T. Narasimhan, *Rev. Sci. Instrum.* **52**, 533 (1981).

⁷K. H. Hausser and D. Stehlik, *Advances in Magnetic Resonance*, edited by J. S. Waugh (Academic, New York, 1968), Vol. 3, p. 79.

⁸R. A. Dwek, R. E. Richards, D. Taylor, and R. A. Shaw, *J. Chem. Soc. A* 1173 (1970).

⁹B. E. Wagner, R. D. Bates, Jr. and E. H. Poindexter, *Inorg*

Chem. **14**, 256 (1975).

¹⁰J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw Hill, New York, 1970), p. 153.

¹¹C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. (London) A* **191**, 39 (1947).

¹²P. A. Dobosh, "CNINDO", Program No. 141, QCPE, Indiana University, Bloomington, Indiana (1974).

¹³M. Iwasaki, *Bull. Chem. Soc. Jpn.* **32**, 194 (1959).

Temporary negative ions in the chloromethanes CHCl_2F and CCl_2F_2 : Characterization of the σ^* orbitals

P. D. Burrow, A. Modelli,^{a)} and N. S. Chiu^{b)}

Department of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111

K. D. Jordan^{c)}

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 23 March 1982; accepted 17 May 1982)

In this work, electron transmission spectroscopy (ETS)¹ is employed to study low-lying temporary anions in the chloromethanes. The resulting electron affinities (E.A.), within the context of Koopmans' theorem, may be associated with the energies of the low-lying unfilled orbitals of these compounds. Such data are of fundamental importance for an understanding of the electronic structure of molecules, and are relevant to studies of fragment anion production by electron capture through the dissociative attachment mechanism, to the interpretation of optical absorption spectra of the neutral molecules, and to electron impact studies of inner-shell electron excitation.

ETS has proven to be a sensitive technique for the study of short-lived anion states formed by capture of electrons into the normally unfilled π^* orbitals of unsaturated hydrocarbons.^{2,3} However, such measurements in small saturated hydrocarbons have been less useful, because the anion states associated with the antibonding orbitals in these systems lie at high energies and have very short lifetimes, and hence, broad widths. In recent work, however, we found that chlorine substitution on ethylene⁴ and benzene⁵ produced additional features in the transmission spectra other than those due to the π^* orbitals. We have attributed these to the filling of low-lying C-Cl σ^* orbitals. In support of this assignment, we expect that similar anion states should exist in the chlorinated alkanes, and in this note we describe our results in the simplest molecules of this class.

In Fig. 1, we present the transmission spectra of the chloromethanes, CHCl_2F , and CCl_2F_2 , plotting the derivative of the unscattered electron current transmitted through the gas cell as a function of electron impact energy.⁶ The vertical arrows below the curves are at the observed midpoints between dip and peak and

correspond to the vertical attachment energies, i. e., the negative of the vertical electron affinities.⁷

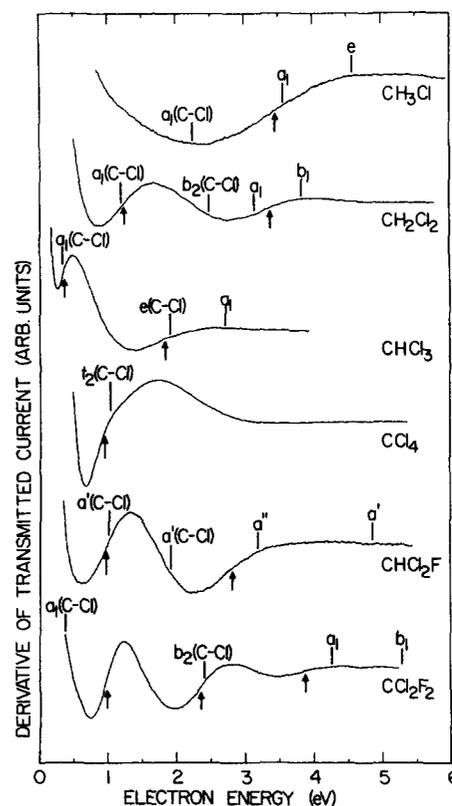


FIG. 1. Derivative of transmitted current as a function of electron impact energy. The vertical arrows beneath the curves locate the vertical attachment energies. The lines above each curve indicate the theoretical anion energies and orbital symmetries. The theoretical energies are normalized to the experimental data only at the 2A_1 resonance in CHCl_3 .