

In the previous study² it appeared that the metastable state involved was $^3\Sigma^+$, with perhaps some $^3\Delta$. In the present case, because the reaction occurs in the ion source and the ions remain in the source approximately 18 μsec , the $^3\pi$ and $^3\Sigma^-$ states may also be involved.

There are several possible processes that may occur in the source to change the "state composition" of the beam. The most likely are excitation transfer, resulting in ground-state ions and excited neutrals, and de-excitation, where the excitation energy goes either to kinetic energy (superelastic collisions) or to radiation. Two other probable processes are elastic scattering and resonant charge transfer. However, neither of the latter processes will affect the beam composition significantly because in the first process the elastic scattering cross sections for the various states will very likely be nearly equal, and in the second the products of the reaction will be the same as the reactants, although the directions of travel may be different.

The apparatus for analyzing the state composition of ion beams has been described in an earlier paper.¹ The ion source used was developed for the present study to provide more precisely defined source parameters, in particular, the path length of the ions (in this case, $1.1 \text{ cm} \pm <10\%$). In the cylindrical ionization region of this source, the electrons travel diametrically and the ions travel axially. An extraction field for the ions is provided by a potential between the cylindrical region and an adjacent source wall and by a potential between the source wall and an extraction lens. In this experiment the NO^+ ions were formed by the impact of 50-eV electrons with neutral NO.

The de-excitation cross section is computed from

$$Q = \frac{\ln(f_0/f)}{nl},$$

where f is the fraction of excited ions in the beam at number density n in the source, f_0 is the fraction of excited ions in the limit of $n=0$, and l is the length of the ion path in the source. Because of the necessary extraction fields, the energy of the ions in the source will vary with an energy bandwidth ΔE . To determine whether the cross section was strongly energy dependent, several experiments were carried out under various source conditions. In addition, because of the relatively simple source geometry, it was possible to calculate the fields inside the source. The optimum operating conditions were obtained by minimizing the extraction fields while still maintaining an ion current adequate for the measurement, thus minimizing ΔE . An analysis of this situation showed that the ions were in the thermal energy region for approximately 80% of the distance traveled in the source. However, this result is only approximate because unknown contact potentials and deviations of the source from the ideal geom-

etry were not taken into account. The data obtained under these conditions and a least-squares fit are shown in Fig. 1, where the fraction of excited ions is plotted semilogarithmically as a function of n . It should be noted that the values of Q obtained from the various experiments remained constant within experimental error, indicating that Q is not strongly energy dependent in this region. The resulting value of Q is $3.3 \pm 2 \times 10^{-15} \text{ cm}^2$, where the uncertainty given is based primarily upon repeatability.

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¹ B. R. Turner, J. A. Rutherford, and D. M. J. Compton, *J. Chem. Phys.* **48**, 1602 (1968).

² R. F. Mathis, B. R. Turner, and J. A. Rutherford, "Abundance of Excited Ions in an NO^+ Ion Beam," *J. Chem. Phys.* (to be published).

Theory of Saturation and Double Resonance Effects in ESR Spectra. IV. Electron-Nuclear Triple Resonance*

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Recent experimental¹⁻³ and theoretical⁴⁻⁶ studies of the ENDOR technique in liquids have demonstrated its utility in analyzing complex ESR spectra and also its strong dependence on the details of spin relaxation. It was predicted that liquid-state ENDOR enhancements are optimum when the lattice induced nuclear-spin-flip rate (W_n) [usually due to an electron-nuclear dipolar (END) mechanism] is comparable to the lattice-induced electron-spin-flip rate (W_e).^{4,5} In a simple picture, this is because "shorting out" W_n between the two spin levels b and d ⁷ makes the relaxation of the saturated $a \leftrightarrow b$ ESR transition occur more rapidly via the alternative path $a \rightarrow c$ (W_n); $c \rightarrow d$ (W_e); $d \rightarrow b$ (rf induced),^{4,7} as long as W_n and W_e are still active. In many liquid situations, particularly near room temperature, one expects $W_e \gg W_n$ for protons, and a very poor ENDOR enhancement is both predicted⁴⁻⁶ and observed.¹⁻³ If, however, *both* nuclear transitions: $\omega_n = |\gamma_n B_0 \pm \frac{1}{2} \gamma_e a_n|$ corresponding to a particular proton (or set of equivalent protons) are *simultaneously* saturated, then it should be possible to obtain significant ENDOR enhancements even when $W_e \gg W_n$,⁴ because now also the $a \rightarrow c$ transition is "shorted out." One could then obtain information equivalent to that of the ENDOR technique, but on a greater variety of samples.

An analysis of such triple resonance effects may be made by a straightforward application of the general

theory of saturation effects in liquids.⁴⁻⁶ The result for the four-level spin system⁷ is that the saturation parameter for ESR, Ω_e , must be replaced in the triple resonance experiment (just as in ENDOR) by $\Omega_e - \xi_e$ where now

$$\xi_e = \frac{d_n^2 \Omega_{e,n}^2 T_n (Y_{n'} + d_{n'}^2 T_{n'} \Omega_{n,n'}) + d_{n'}^2 \Omega_{e,n'}^2 T_{n'} (Y_n + d_n^2 T_n \Omega_{n,n'})}{Y_n Y_{n'} - d_n^2 d_{n'}^2 \Omega_{n,n'}^2 T_n T_{n'}} \quad (1)$$

and $Y_n = 1 + T_n^2 \Delta\omega_n^2 + T_n \Omega_n d_n^2$ with an equivalent equation for $Y_{n'}$. The notation is the same as that of the earlier papers,⁴⁻⁶ with subscripts n and n' referring to the two induced NMR transitions, and ξ_e gives the effective reduction in the saturation parameter. Coherence effects of the radiation field of the type discussed in Ref. 6 are neglected in Eq. (1), and conditions similar to Eqs. (3.1)-(3.3) of Ref. 6 for the validity of this neglect are expected. Under the simplifying assumptions that $\Delta\omega_n = \Delta\omega_{n'} = 0$ (NMR frequencies at resonance) and

$$d_n^2 T_n \Omega_n, \quad d_{n'}^2 T_{n'} (\Omega_n \Omega_{n'} - \Omega_{n,n'}^2) / \Omega_{n'} \gg 1, \quad (2)$$

as well as the other pair of inequalities resulting from interchanging the indices n and n' (these define "effective" saturation of both NMR transitions; note however that the transition moments d_n and $d_{n'}$ are generally unequal⁴), then one has in terms of saturation and cross-saturation parameters,

$$\xi_e^r(d_n, d_{n'} \rightarrow \infty) = [\Omega_{e,n}^2 (\Omega_{n'} + \Omega_{n,n'}) + \Omega_{e,n'}^2 (\Omega_n + \Omega_{n,n'})] / (\Omega_n \Omega_{n'} - \Omega_{n,n'}^2).$$

(The equivalent result for the ENDOR is $\Omega_{e,n}^2 / \Omega_n$.) The new term $\Omega_{n,n'}$ gives the saturation coupling of the two NMR transitions. If it is also assumed that the only important relaxation mechanisms are the nuclear-spin-independent W_e (e.g., g -tensor and spin-rotational contributions), the pseudosecular part of the END interaction yielding W_n , and exchange processes with total frequency ω_E ,^{4,5} then one obtains $\Omega_e - \xi_e^r(\infty) = \Omega_e [1 - W_e / (2W_e + W_n + \frac{1}{2}\omega_E)]$, where Ω_e is given in Table I of Ref. 5. This expression shows that there will be a significant reduction in the saturation parameter as a result of applying both NMR fields, if

$$W_e \gtrsim W_n, \quad \frac{1}{2}\omega_E. \quad (3)$$

If $W_e \gg W_n, \frac{1}{2}\omega_E$, then the reduction is by a factor of 2 corresponding to a maximum possible signal enhancement of the saturated ESR of 100% (as compared with an 11% maximum enhancement for ENDOR occurring when $W_e = W_n \gg \omega_E$). A similar analysis for systems with more than one equivalent proton shows even

greater enhancements are possible when Eq. (3) holds (e.g., for a single nuclear spin of $I=1$, or for the $J=1$ components of two equivalent nuclear spins of $I=\frac{1}{2}$, values up to 200% are possible).

By "effective" saturation associated with Eqs. (2) we do not specifically refer to the actual saturation of an NMR absorption (which could also be readily analyzed utilizing the general theories⁴⁻⁶), but rather the "shorting-out" effect has seen by monitoring the (partially) saturated ESR absorption. The second inequality of Eq. (2) results, in fact, from the coupled effects of both induced NMR absorptions, and when Eq. (3) is appropriate it becomes the condition limiting "effective" saturation. It may then be written as $4d_n^2 T_n (2W_n + W_e + \frac{1}{2}\omega_E)^{-1} \gg 1$. Thus, when W_e is the dominant spin-relaxation term, it determines the condition of "effective" saturation. And, even though the "relaxation time" Ω_n (which is roughly of the order of W_n^{-1} ^{4,5}) may be very long, substantial rf fields would still be required to fulfill this inequality.⁸ This situation is different from simple ENDOR, wherein the "effective" NMR saturation is determined just by the first inequality of Eq. (2), hence on Ω_n . Thus, while it would, in principle, be easier to achieve "effective" saturation for ENDOR as compared to triple resonance when $W_e \gg W_n, \frac{1}{2}\omega_E$, the limiting ENDOR enhancements would be very small, while for triple resonance they would be large, as we have already noted.

One might expect to perform the experiment by amplitude modulation by a variable rf of a constant rf equal to the free proton resonance, so that both NMR resonances are reached simultaneously when the variable rf just equals half the hyperfine splitting. The experiment would probably require resonant coupling of the rf power to the rf coils for *both* NMR frequencies.⁹

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⁴ J. H. Freed, *J. Chem. Phys.* **43**, 2312 (1965).

⁵ J. H. Freed, *J. Phys. Chem.* **71**, 38 (1967).

⁶ J. H. Freed, D. S. Leniart, and J. S. Hyde, *J. Chem. Phys.* **47**, 2762 (1967).

⁷ The notation here is for a four-level spin system arising from an unpaired electron interacting with a single spin of $I=\frac{1}{2}$. Eigenstates are abbreviated $(++)=a$, $(-+)=b$, $(+-)=c$, and $(--)=d$ in the notation $(M_x M_I)$.

⁸ When Eq. (3) holds, it is easily seen from Eq. (1) and the appropriate expressions for the saturation parameters⁴⁻⁶ that the *unsaturated* NMR condition *cannot* yield significant triple resonance enhancements.

⁹ R. J. Cook and D. H. Whiffen, *Proc. Roy. Soc. (London)* **84**, 845 (1964), describe a *solid-state* experiment involving simultaneous irradiation of two NMR resonances, but corresponding to *different* proton hyperfine splittings.