$$B=\frac{B}{D^{-1}}D^{-1}=\frac{D^{-1}}{(B+D)/B}=\frac{D^{-1}}{1+D/f'_{\rm feed}C^{-1}}\;. \tag{B1}$$

Dividing the traps into shallow (1) and deep (2) traps as in Appendix A, the $D/f'_{\rm feed}C^{-1}$ denominator term becomes

$$\frac{D_1+D_2}{f'_{\rm feed}C^{-1}}=\left(\frac{D_1}{D_2}+1\right)\frac{D_2}{f'_{\rm feed}C^{-1}}=\frac{\delta+1}{\hat{n}_0}\;, \tag{B2}$$

where

$$\delta=\frac{D_1}{D_2}=\frac{\langle\sigma_{p1i}\rangle N_{1\,\rm trap}}{\langle\sigma_{p2i}\rangle N_{2\,\rm trap}}\;. \tag{B3}$$

The Eu^{+2} concentration $n_0(t)$ and the trapped-hole concentrations decrease slowly when excitation is removed. Thus,

$$\hat{n}_0(t)=\hat{n}_0(0)\alpha_0(t),\quad D_1^{-1}(t)=D_1^{-1}(0)\alpha_1(t),$$
$$D_2^{-1}(t)=D_2^{-1}(0)\alpha_2(t)\;, \tag{B4}$$

where $\alpha_0(t)$, $\alpha_1(t)$, and $\alpha_2(t)$ decrease slowly from unity and

$$\hat{n}_0(0)=\hat{n}_{0\infty},\quad D_1^{-1}(0)=D_{1\infty}^{-1}=D_{1\infty}=\delta\,D_{2\infty},$$
$$D_2^{-1}(0)=D_{2\infty}^{-1}\equiv(\epsilon/\hat{n}_{0\infty})D_{2\infty}\;. \tag{B5}$$

The deep-trap constant ϵ is given by

$$\epsilon\equiv\hat{n}_{0\infty}D_{2\infty}^{-1}/D_{2\infty}$$
$$=\langle\sigma_{p2i}\bar{p}_{2i}/e_{2i}\rangle v_T\,f'_{\rm feed}\sigma_{p0}/\langle\sigma_{p2i}\rangle^2N_{2\,\rm trap}\;. \tag{B6}$$

The slow-time dependences $\alpha_0(t)$, $\alpha_1(t)$, and $\alpha_2(t)$ will not need to be known accurately since our main concern lies with the G dependence of the early phosphorescence.

Introducing Eqs. (B2), (B4), and (B5) into Eq. (B1), the phosphorescence B_P becomes

$$B_P(t)=\frac{\delta\alpha_1(t)+(\epsilon/\hat{n}_{0\infty})\alpha_2(t)}{1+(\delta+1)/\hat{n}_{0\infty}\alpha_0(t)}\,D_{2\infty}\;. \tag{B7}$$

The $\alpha_1(t)$ and $\alpha_2(t)$ decrease as the traps empty. The $\alpha_0(t)$ decrease expresses the effect of a given amount of detrapping producing less emission as the Eu^{+2} concentration n_0 decreases. Recalling that $D_{2\infty}=E_\infty$ and using Eq. (A6), one obtains

$$\frac{B_P(t)}{G}=\frac{f'_{\rm ionize}}{1+\hat{n}_{0\infty}}\,\frac{\delta\alpha_1(t)+(\epsilon/\hat{n}_{0\infty})\alpha_2(t)}{1+(\delta+1)/\hat{n}_{0\infty}\alpha_0(t)}\;. \tag{B8}$$

Equation (B8) was quoted in the text as Eq. (9).

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[1] C. W. Struck and W. H. Fonger, in *Extended Abstracts, the Electrochemical Society, Spring Meeting, Los Angeles, California, May* 10–15, 1970 (The Electrochemical Society, New York, 1970), p. 119; W. H. Fonger and C. W. Struck, J. Electrochem. Soc. 118, 273 (1971).

[2] H. Forest, A. Cocco, and H. Hersh, Electrochemical Society, Boston Meeting, RNP 300, 1968 (unpublished).

[3] H. Forest, A. Cocco, and H. Hersh, J. Luminescence 3, 25 (1970).

[4] C. W. Struck and W. H. Fonger, J. Luminescence 1/2, 456 (1970).

[5] W. H. Fonger and C. W. Struck, J. Chem. Phys. 52, 6364 (1970).

[6] Sublinear, in this paper, means varying as G^α with $\alpha<1$. Similarly, superlinear means varying as G^α with $\alpha>1$. In both cases α need not be constant.

[7] R. N. Hall, Phys. Rev. 87, 387 (1952).

[8] W. Shockley and W. T. Read, Phys. Rev. 87, 835 (1952).

[9] K. A. Wickersheim, R. A. Buchanan, and E. C. Yates, in Proceedings of the Seventh Rare-Earth Research Conference, Coronado, Calif., 1968, p. 835 (unpublished).

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Annihilation of Positrons in Methane*

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Positron lifetime spectra have been measured in methane gas at 23 °C over a density range of 5.0×10^{-4} to 1.5×10^{-2} g/cm^3. Statistical analysis of the data yields a ${}^1Z_{\rm eff}$ of 0.442 ± 0.019 for orthopositronium and a $Z_{\rm eff}$ of 153.3 ± 0.6 for positrons which do not form positronium. Several annihilation mechanisms are discussed in connection with the data.

INTRODUCTION

The annihilation of positrons has been investigated in many different monatomic and simple diatomic gases, and considerable progress has been made in the theoretical interpretation of the observed annihilation processes.[1] However, relatively few experimental investigations have been concerned with positrons annihilating in polyatomic gases. The scarcity of experimental data, coupled with the greater complexity of the involved interactions, has hindered theoretical research into the annihilation mechanisms available to positrons injected into polyatomic gases.

We have recently begun an investigation of the annihilation of positrons in methane gas as a function of gas density and temperature. It was felt that a comprehensive study of the interactions of positrons with such structurally simple polyatomic gas molecules would provide a logical approach to the understanding of positron annihilation in all polyatomic gases. In this paper we report measurements made at (23 ± 1) °C over a density range of 5.0×10^{-4} to 1.5×10^{-2} g/cm^3.

EXPERIMENTAL

Research-grade methane gas, supplied by Matheson Gas Products, was used throughout the experiment. The gas had a purity of 99.8 mole% as determined by mass spectrometry. The following analysis of maximum impurities, as certified by the supplier for one cylinder, was typical: CO_2, 10 ppm; O_2, 6 ppm; N_2, 15 ppm; C_2H_6, 22 ppm; C_3H_8, 5 ppm.

The gas-handling system, which utilized tubing connectors with metal packings, was constructed entirely of stainless steel. Two cylindrical stainless-steel gas chambers were used in the measurements. A vessel having an inside diameter of 5.6 in. and a height of 7.6 in. was used for low gas densities. For high gas densities, a 2.4-in.-diam 4.8-in.-high vessel was used. These chambers were initially sealed with Buna-N O rings, but when they were later converted to threaded seals, no difference in positron or orthopositronium mean lives was detected.

In order to prevent the introduction of impurities into the gas, extreme care was taken in the initial cleaning of the gas system and repeated flushings of the system were performed prior to the introduction of a final gas sample. Additionally, new gas samples were introduced frequently.

The positron sources were prepared by depositing several microcuries of a high-specific-activity ^{22}NaCl solution on 1.75-mg/cm^2 Mylar film and evaporating to dryness. The ^{22}Na sources, which appeared as stains on the Mylar films, were centered in the gas chambers by small stainless-steel source holders.

The annihilation lifetime spectra were measured with a standard type of timing spectrometer which utilized fast photomultiplier tubes, two time-to-pulse-height converters covering different time ranges, and a 512-channel multichannel analyzer. Typical time-resolution values were as follows: the full width at half-maximum of a ^{60}Co prompt peak was about 0.6 nsec on the 50-nsec time scale and was about 5 nsec on the 1000-nsec time scale. Other intermediate time ranges, with intermediate time resolutions, were employed where advantageous.

The measured lifetime spectra were resolved into two components by a weighted nonlinear least-squares computer fit to two exponentials.[2] The component characterized by the longer lifetime arose from the annihilation of orthopositronium

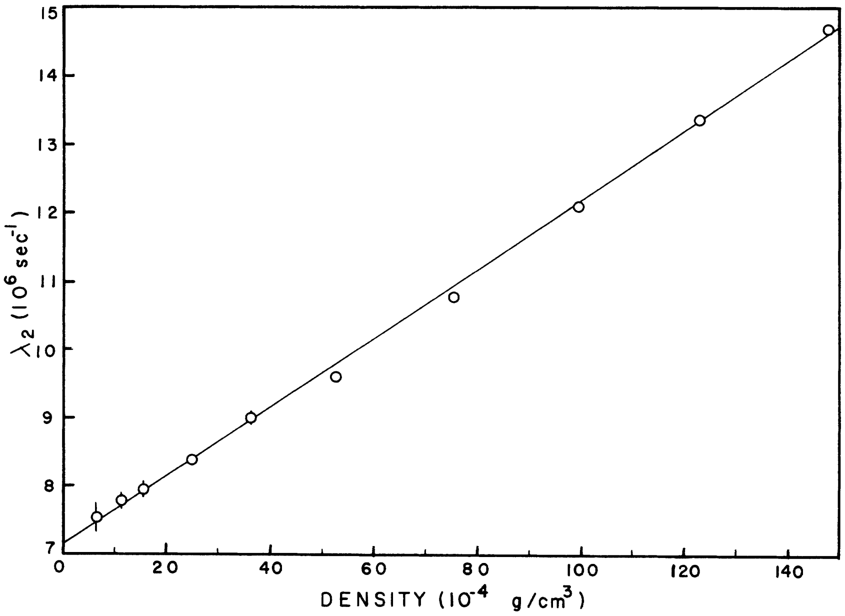

FIG. 1. Orthopositronium annihilation rate versus methane gas density at room temperature. The estimated errors in density and the statistical standard deviations in the annihilation rates fall within the circles unless otherwise indicated. Several low-density points have been omitted for clarity. The solid line represents a weighted least-squares fit to all the data.

while the other, shorter-lived component was attributed to the annihilation of either free thermalized positron or positrons forming some type of complex with one or more methane molecules.

RESULTS AND DISCUSSION

Orthopositronium in Methane

The room-temperature orthopositronium annihilation rate λ_2 as a function of methane gas density is presented in Fig. 1. A statistically weighted least-squares fit to the data is shown as a solid line. The zero-density intercept of the line, (7.16 ± 0.03) μsec^{-1}, is in agreement with the theoretical value of 7.2 μsec^{-1}.[3]

The slope of the orthopositronium annihilation rate-vs-density line is (0.503 ± 0.004) $\text{cm}^3/\text{g nsec}$. The data correspond to

$$ {}^1Z_{\text{eff}} = 0.442 \pm 0.019 , $$

where ${}^1Z_{\text{eff}}$ is the effective number of electrons per molecule which are available for singlet annihilation with the positron of the orthopositronium atom.[4] ${}^1Z_{\text{eff}}$ is determined from the equation

$$ \lambda_2 = 7.2 \times 10^6 \text{ sec}^{-1} + (4\pi r_0^2 c)(\rho/M)\, {}^1Z_{\text{eff}} , \qquad (1) $$

where r_0 is the classical electron radius, c is the speed of light, and ρ and M are the molecular density and mass, respectively.

The ratio of ${}^1Z_{\text{eff}}$ to the atomic number, $Z = 10$, of methane is 0.044. This compares with a ${}^1Z_{\text{eff}}$ to Z ratio for argon,[5] nitrogen,[5] hydrogen,[6] and carbon dioxide[6] of 0.019, 0.02, 0.054, and 0.017, respectively. There appears to be no other value in the literature for the orthopositronium annihilation rate in methane.

The orthopositronium annihilation rate-vs-density plot was also examined for an indication of positronium-induced cavity formation as has been observed in helium[7] and hydrogen[8] gas. This effect has been attributed to the repulsive exchange potential which exists between the positronium atom and the gas molecules. The formation of cavities, where energetically possible, might be expected to occur most readily with symmetric molecules where the exchange potential would be essentially independent of the orientation of the molecule in its collision with the positronium atom. This phenomenon would be indicated by a deviation from linearity of the orthopositronium annihilation rate-vs-density plot at low densities due to collapse of the cavities. As is shown in Fig. 2, no anomalous behavior in annihilation rate was noted down to a density of 4.96×10^{-4} g/cm^3 (0.69 amagat), the lowest density at which measurements were made. Certainly, measurements must be taken at lower densities in order to fully investigate this effect.

Slow Positrons in Methane

The room-temperature annihilation rate of positrons which do not form positronium, λ_1, as a function of gas density is presented in Fig. 3. A statistically weighted least-squares fit to the data, shown as a solid line, resulted in a zero-density intercept of about 2.6×10^{-4} nsec^{-1} and a slope of (43.21 ± 0.24) $\text{cm}^3/\text{g nsec}$. The data correspond to

$$ Z_{\text{eff}} = 153.3 \pm 0.6 , $$

where Z_{eff} is the effective number of electrons per molecule available for singlet annihilation.[4] Z_{eff} is determined from the equation

$$ \lambda_1 = (\pi r_0^2 c)(\rho/M) Z_{\text{eff}} , $$

where the symbols have the same meaning as in Eq. (1). This compares reasonably well with the Z_{eff} of 162 ± 4 determined by Paul and Saint-Pierre for methane partial pressures less than one atmosphere.[9] This latter value, which appears to be the only one reported in the literature, was obtained

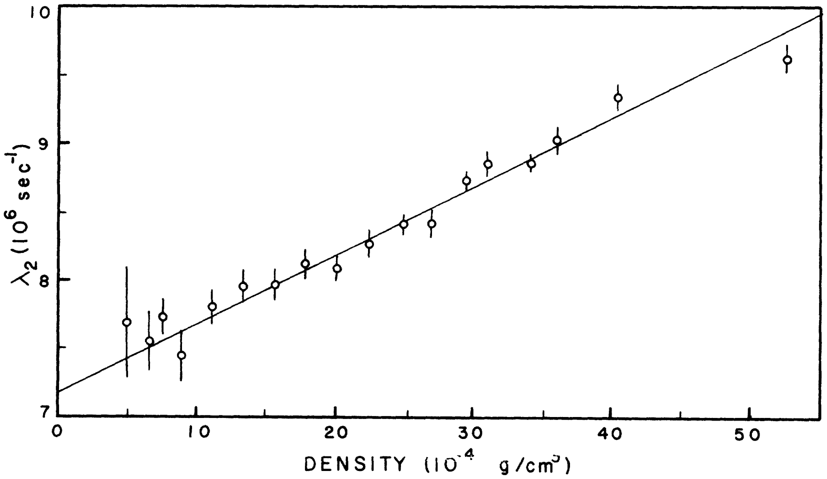

FIG. 2. Room-temperature orthopositronium annihilation rate versus methane gas density at low densities. The estimated errors in density and the statistical standard deviations in the annihilation rates fall within the circles unless otherwise indicated. The solid line represents the weighted least-squares fit of Fig. 1.

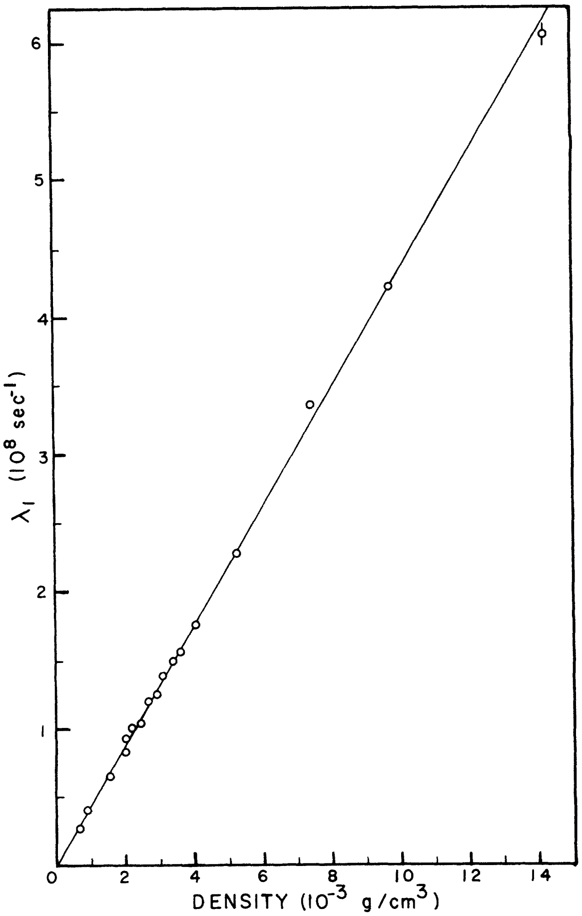

FIG. 3. Annihilation rate of positrons which do not form positronium versus methane gas density at room temperature. The estimated errors in density and the statistical standard deviations in the annihilation rates fall within the circles unless otherwise indicated. The solid line represents a weighted least-squares fit to the data.

with small partial pressures of methane in an argon background with small amounts of nitric oxide added to quench the orthopositronium lifetime.

The experimentally determined $Z_{\rm eff}$ is over 15 times the atomic number, $Z = 10$, of methane and is about 10.5 times the value calculated for methane from the average atomic $Z_{\rm eff}$'s for carbon and hydrogen determined by Cova and Zappa from annihilation measurements in a number of different materials.[10] Additionally, the ratio of the experimentally determined annihilation rate per density to the molecular polarizability of methane is considerably higher than that predicted from an empirical fit to a series of other molecular gases reported by Osmon.[6] It is apparent that the observed annihilation rates in methane do not represent only the direct annihilation of free positrons, but involve more complex modes of annihilation. The high $Z_{\rm eff}$ measured for methane has been attributed to the resonance annihilation of positrons in virtual positron-gas molecular states.[11] Preliminary measurements with methane at temperatures other than 23 °C, however, indicate that free-positron annihilation at room temperature may not be primarily influenced by virtual-state formation.[12]

The formation of electrorestricted clusters of gas molecules about low-energy positrons has been postulated for helium.[13,14] The onset of cluster formation requires that the positron be initially localized. If the large $Z_{\rm eff}$ measured in methane is produced by the clustering of methane molecules about the positron, the required localization may well result from the formation of a positron-methane compound.

The lifetime spectra in methane were examined for the presence of a shoulder indicating a long positron-thermalization time due to the availability of only elastic collisions below positron energies of 0.16 eV and, hence, a sizable probability of annihilation prior to thermalization. Since the shoulder width is inversely proportional to the gas pressure,[15] a shoulder would be most prominent at low pressures and on a short time range. Accordingly, a lifetime spectrum was obtained at 380 Torr (0.46 amagat), the lowest pressure which yielded an acceptable counting rate, and on the 50-nsec time range, the shortest available time range. No indication of a shoulder was observed in the spectrum, indicating that the thermalization time of positrons in methane at this pressure must be less than about 1 nsec. This result is in qualitative agreement with the thermalization time of 0.25 nsec reported by Paul and Leung for ^{22}Na positrons injected into methane at a density of 1 amagat.[15] For positrons in the energy range below 0.16 eV, the rapid energy-loss mechanism is unknown. Here again is indication of more complex positron-methane interactions.

Measurements of positron annihilation in methane at different temperatures and higher densities, as well as in other simple polyatomic gases, should provide additional insight into the nature of the annihilation mechanisms.

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[*] Work supported in part by The Robert A. Welch Foundation, Houston, Tex.

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[1] See, for example, J. Green and J. Lee, *Positronium Chemistry* (Academic, New York, 1964); in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967); P. A. Fraser, Advan. At. Mol. Phys. 4, 63 (1968).

[2] S. J. Tao, IEEE NS-15 1, 175 (1968). The computer program is a modified version of a program developed by S. J. Tao, J. C. Miller, and G. J. Celitans (private

communication).

[3] A. I. Alekseev, Zh. Eksperim. i Teor. Fiz. 36, 1839 (1959) [Sov. Phys. JETP 9, 1312 (1959)].

[4] P. A. Fraser, Advan. At. Mol. Phys. 4, 63 (1968).

[5] C. J. Celitans and J. H. Green, Proc. Phys. Soc. (London) 83, 823 (1964).

[6] P. E. Osmon, Phys. Rev. 140, A8 (1965).

[7] L. O. Roellig and T. M. Kelly, Phys. Rev. Letters 18, 387 (1967).

[8] K. F. Canter, J. D. McNutt, and L. O. Roellig, Bull. Am. Phys. Soc. 14, 89 (1969).

[9] D. A. L. Paul and L. Saint-Pierre, Phys. Rev. Letters 11, 493 (1963).

[10] S. Cova and L. Zappa, J. Phys. B 1, 795 (1968).

[11] V. I. Goldanskii and Yu. S. Sayasov, Phys. Rev. Letters 13, 300 (1964).

[12] J. D. McNutt, V. B. Summerour, and D. A. Johnson (unpublished).

[13] L. O. Roellig, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 127.

[14] L. O. Roellig and J. D. McNutt, Bull. Am. Phys. Soc. 13, 634 (1968).

[15] D. A. L. Paul and C. Y. Leung, Can. J. Phys. 46, 2779 (1968).

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Antisymmetric Exchange and Exchange-Narrowed Electron-Paramagnetic-Resonance Linewidths*

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The Dzialoshinsky-Moriya (DM) antisymmetric exchange interaction between superexchange-coupled ions in antiferromagnetic salts is shown to contribute to the exchanged-narrowed electron-paramagnetic-resonance (EPR) linewidth in the paramagnetic state. The contribution of antisymmetric exchange to the second and fourth moments has been calculated and is analogous to that from symmetric anisotropic exchange and the dipole–dipole interaction. It is demonstrated that for $Cu(HCOO)_2 \cdot 4H_2O$, both the linear temperature dependence of the EPR linewidth and the temperature-independent exchange-narrowed linewidth (extrapolated to $T = 0$ °K from the paramagnetic region where $kT > J$) can be explained by the DM antisymmetric exchange interaction and are mutually consistent with one another. The analysis yields a value of the antisymmetric exchange $|\mathfrak{D}_{jk}|/g\mu_B$ for $Cu(HCOO)_2 \cdot 4H_2O$ of order 2700 Oe and a second moment M_2 more than two orders of magnitude larger than the contribution to M_2 from the dipole-dipole interaction. Several other magnetic salts where the DM antisymmetric exchange interaction might contribute to the EPR linewidth are considered.

I. INTRODUCTION

In magnetic insulators with large exchange interactions, the electron-paramagnetic-resonance (EPR) linewidth is exchange narrowed. This phenomenon has been successfully described by the theories of Anderson and Weiss[1] and Kubo and Tomita.[2] These theories predict a frequency width of order ω_p^2/ω_e, where ω_e is the exchange frequency and ω_p^2 is the frequency second moment[3] of the EPR line shape due to various spin-spin interactions. Ordinarily it is the dipole-dipole interaction between spins which accounts for ω_p^2; however, it is also possible for symmetric anisotropic exchange terms[4] and crystal field fine-structure terms[5] to contribute to ω_p^2.

Crystals having large superexchange interactions (antiferromagnets) as well as sufficiently low symmetry[6] contain antisymmetric exchange terms resulting from the Dzialoshinsky-Moriya (DM) interaction.[7] The DM antisymmetric exchange interaction is known to account for the weak ferromagnetism of certain superexchange-coupled magnetic crystals and also to play an important role in the antiferromagnetic-resonance (AFMR) modes of such crystals. However, the role of antisymmetric exchange terms on the EPR linewidth has received little attention. Moriya has shown[7] that the magnitude (symmetry permitting) of the antisymmetric exchange should be of order $(\Delta g/g)J$, while the symmetric anisotropic exchange terms should be of order $(\Delta g/g)^2 J$, where g is the g shift and J the magnitude of the isotropic exchange interaction. Thus low-symmetry antiferromagnets with large exchange and sizable g shifts can produce a situation whereby the largest anisotropic exchange interaction is antisymmetric and can be larger than the dipole-dipole interaction. Because of their appreciable g shifts, copper salts which possess large exchange interactions are cases where antisym-