THE TWENTY-TWO MOST FREQUENTLY CITED APL PUBLICATIONS — II

In the late 1920s, chemists began to realize that, in addition to the myriads of stable (that is, stable at room temperature) chemical structures, there existed a world of short-lived substances whose presence could be deduced at that time from a few ingenious experiments and theories. Twenty years later, these so-called "free radicals" were firmly established. Their general involvement in many, if not most, chemical reactions of gases was well documented. However, little was known about their formation and disappearance in reacting systems, such as flames, or, because of their short lifetimes, about their physical properties.

APL research was deeply involved with the reaction rates of free radicals. Even though the radicals were rapidly reacting with themselves or with other substances in proximity, the rates were measurable, as demonstrated in a series of articles in the preceding issue of the *Johns Hopkins APL Technical Digest.*

The following group of papers deals with two different aspects of free-radical physics: the isolation of a particularly elusive species (the hydroperoxyl radical) when generated under favorable conditions and the investigation of physical properties when the free radicals were immobilized by incorporating them into a solid matrix at a very low temperature where no further reactions were possible. Once the techniques were developed, both strands of research were applied to a wide variety of free radicals. Because of the utility of the methodology, the papers were widely cited by colleagues who adapted them to their own interests.

WALTER G. BERL

FREE RADICALS ENTRAPPED

CHIH KUNG JEN

C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, "Electron Spin Resonance of Atomic and Molecular Free Radicals Trapped at Liquid Helium Temperature," *Phys. Rev.* **112,** 1169-1182 (1958).

In the early 1950s, a group of us (C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers) felt very strongly that reactive chemical free radicals with normally very short lifetimes could be stabilized so that they could be studied at leisure with some sort of physical instrumentation. The idea of trapping relatively small radicals in an inert-gas solid matrix at a low temperature appeared promising, and detecting free radicals by electron spin resonance techniques appealed to us because we had the necessary experience and know-how of electron spin resonance techniques to accomplish such a project. Early in 1956, we began the experiment. Shortly thereafter, in September 1956, we reported to the Symposium on Free Radicals held at Laval University in Quebec, Canada, the successful trapping of hydrogen atoms in a solid hydrogen matrix at liquid helium temperatures. That initial success was followed by the trapping of deuterium atoms in a deuterium matrix, nitrogen atoms in a hydrogen matrix, and nitrogen dioxide and methyl radicals in a solid argon matrix. The electron spin resonance spectrum of each radical was interpreted by applying appropriate theories on the g-factor, hyperfine structure, and spin-lattice relaxation mechanisms. The article "Electron Spin Resonance of Atomic and Molecular Free Radicals Trapped at Liquid Helium Temperature" was a summary of the work up to that time.

We became aware of the public interest in that paper because of the large number of requests for reprints, for scale drawings of our radical deposition system, and for other details of our work. But we did not follow its citation history until we were told about it much later.

What could have been the reason for our work having produced such a favorable effect on the technical community? My own guess follows.

The idea of trapping transient and normally short-lived highly reactive chemical free radicals had been

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Electron Spin Resonance of Atomic and Molecular Free Radicals Trapped at Liquid Helium Temperature*

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Electron spin resonance spectra of H, D, N, and CH_3 trapped in solid matrices at liquid helium temperature have been observed and interpreted. The effect of the matrix field on the resonance properties of the radicals has been investigated by depositing the radicals in matrices with different binding energies. The effect of the matrix on the g factor is extremely small in all cases. The deviation of the hyperfine coupling constant from the free-state value increases in a systematic way with increase in binding energy of the matrix, the percentage deviations being small for H, D, and CH_3 but rather large for the case of N. The widths and shapes of the spectral lines are discussed in terms of dipolar broadening, spin-lattice relaxation, anisotropic broadening, rate of passage and the modulation parameters used for observation.

Complex spectra, not adequately identified, have been observed from discharges in hydrogen and hydrogen-oxygen systems. Deductive evidence for an HO_2 resonance spectrum is presented.

The stable molecular free radicals O_2, NO, and NO_2 have been studied. Only NO_2 yielded a positive result. Resonances for oxygen and chlorine atoms have been sought but not observed. It is suggested that radical species with orbital angular momenta may escape spin resonance observation because of matrix field anisotropy and that radical species with an even number of electrons may be unobservable because of crystalline field splitting resulting in a singlet ground level.

I. INTRODUCTION

FREE radicals trapped in solid media can be generated *in situ* by irradiation (uv, x-ray, γ-ray, electron, neutron, etc.) or can be generated in the gaseous state and subsequently deposited in a suitable matrix. While the technique of stabilizing free radicals by isolating them in a rigid matrix is not new[1] and many frozen chemical systems have been examined for free radicals, the problem of detecting and identifying intermediates in a solid is complicated by matrix interactions, and only a few trapped free radicals have been identified with certainty. The spectra obtained with high-energy radiations, while quite interesting from a radiation damage standpoint, are not so readily interpretable as those obtained either by uv irradiation of the solid or by deposition from the gas state of systems whose radical content has been studied by other methods.

Electron spin-resonance techniques have been applied with great effectiveness to the study of trapped free radicals. The resonance method is inherently selective in detecting only those species with unpaired electron spins. Hyperfine structure in the resonance spectrum frequently permits an unambiguous identification of a free radical. However, there are many instances where the resonance spectra by themselves are inadequate to determine the identity of free radicals.

In this paper, electron spin resonance studies of a number of atomic and molecular free radicals trapped at liquid helium temperature are presented. The effect of the trapping matrix on the resonance spectra is examined. Also discussed are the instances where the resonance approach, as currently applied, has failed to give a positive result.

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II. EXPERIMENTAL

A. Production of Free Radicals

Atomic and simple molecular free radicals are rather easily generated by electric discharges in appropriate gases. As the free radicals being studied increase in complexity, more selective methods of radical production, such as photolysis or photosensitization are needed to obtain specific radicals. While we have used all of the above methods for free radical production, the principal method for the simple free radicals reported here was the electric discharge.

The free radicals were produced by an "electrodeless" discharge in a rapidly flowing gas stream. Two strips of aluminum foil wrapped around the quartz discharge tube (25-mm diameter) coupled the energy from an 8-Mc/sec transmitter into the gas. The power input to the discharge depended on the gases used and was set considerably higher for atom production, roughly 100 watts, than for production of molecular free radicals. The discharge products were pumped by a liquid nitrogen trapped mercury diffusion pump and forepump at a speed of about 1500 cm/sec past a short side tube connected to the low-temperature cell. The side tube was terminated by a glass slit which served as the source slit for a simple molecular beam system. The gas pressure in the discharge varied, depending on the particular experiment and on the size of the glass slit, but was usually about 0.1 mm Hg.

B. Low-Temperature Cell and Sample Deposition System

The general arrangement of the discharge system and the low-temperature cell is shown in Fig. 1. The upper

[1] G. N. Lewis and D. Lipkin, J. Am. Chem. Soc. 64, 2801 (1942).

kicking around for quite some time, but until the time of our publication it had not been realized. Our work may have supplied a creditable pathway that allowed a good idea to go at last to demonstrable reality.

Despite the many powerful applications of electron spin resonance since its invention in 1946, it had not reached the doors of the low-temperature regime of trapped free radicals. Some people may have been impressed by the extension of this important tool. To a theorist, in particular, the fact that an electron spin resonance spectrum can assign the unpaired electron density of the electron to a given magnetic nucleus (there may be several magnetic nuclei in an organic molecule) provides very important and much needed information.

Norman Ramsey, then at Harvard and the inventor of the hydrogen maser, told me a number of times that the lifetime of hydrogen atoms bouncing around from wall to wall in the maser chamber was inferred from our results on the small deviations of the hyperfine constant A and the g-factor of hydrogen atoms in the trapped state. Our data on A and g gave him confidence that hydrogen atoms in a maser would not be too "lossy" and recombine too rapidly.

Hydrogen atoms have been considered to be an ideal fuel for a jet engine in aerospace applications. Standard equations for engine thrust indicate that thrust is inversely proportional to the square root of the atomic (or molecular) weight of the ejected gas. From this it is clear that if hydrogen atoms could be stabilized in reasonably high concentrations, they would provide a very high thrust if allowed to recombine in the rocket chamber and be ejected as molecular hydrogen gas. This possibility gave rise to speculations about hydrogen atoms as fuels, and the news media gave considerable attention to the idea. But enthusiasm died away quickly when it was realized that the hydrogen atom concentration that could reasonably be expected to be stabilized was orders of magnitude below what was needed. Our experimental data showed decisively that the use of hydrogen atoms for jet thrust in rocket engines was not practical.

SPECTROSCOPY OF NOT-SO-FREE RADICALS

FRANK J. ADRIAN and EDWARD L. COCHRAN

F. J. Adrian, E. L. Cochran, and V. A. Bowers, "ESR Spectrum and Structure of the Formyl Radical," *J. Chem. Phys.* **36**, 1661-1672 (1962).

E. L. Cochran, F. J. Adrian, and V. A. Bowers, "ESR Study of Ethynyl and Vinyl Free Radicals," *J. Chem. Phys.* **40**, 213-220 (1964).

A rather intense program of research in early 1956 led to the detection of electron spin resonance spectra for hydrogen atoms, nitrogen atoms, nitrogen dioxide, and methyl radicals stabilized at 4 K in various inert matrices. With these encouraging results, we turned our attention to a systematic exploration of the potential of low-temperature electron spin resonance spectroscopy as a tool for studying reactive free radicals.

The experiments, designed to produce specific radicals cleanly and in good yield, generally involved photochemical reactions that were well understood from work in the gas phase. While some anomalies were encountered in the low-temperature photolyses in solid matrices, the systems nevertheless provided relatively well-defined chemistry. Instrumentation was developed to provide good sensitivity under conditions that permitted line shapes to be analyzed rigorously. With these improvements and certain others, an extensive series of simple radicals of long-standing interest was isolated, identified, and studied in the years that followed.

We found that many small polyatomic free radicals had strong, well-resolved electron spin resonance spectral lines despite the fact that these magnetically anisotropic species are randomly oriented in the solid matrices. In some cases, the spectra were actually isotropic because the radical could rotate (or, more accurately, tunnel quantum mechanically) between different orientations. However, even nonrotating anisotropic radicals had sharp line features in their electron spin resonance spectra, and theory showed that the features were both expected and directly related to the magnetic parameters of the radical. In many cases, temperature changes in the range of 4 to 30 K produced dramatic changes in the appearance of the spectra as the trapped radicals acquired enough energy to rotate and to average out magnetic anisotropies.

Two of the papers published during the period were particularly well received by the scientific community. The first reported the detection and identification of the electron spin resonance spectrum of the formyl radical (CH = O). Analysis of the spectrum clearly placed the unpaired electron in an inplane orbital, rather than in a perpendicular orbital as is characteristic of most organic radicals. It settled conclusively an ongoing argument in the literature about the structure of the formyl radical. The paper contained a particularly useful analysis of electron spin resonance line shapes for ran-

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ESR Study of Ethynyl and Vinyl Free Radicals*

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ESR spectra have been observed for ethynyl (C≡CH) and vinyl (HC=CH_2) radicals trapped in solid argon at liquid-helium temperatures. Ethynyl radical was obtained by the photolytic decomposition of acetylene. Its ESR spectrum consisted of two narrow lines corresponding to a proton hyperfine splitting of 16.1 Oe. The assignment of this spectrum to ethynyl was confirmed by a study of the photolysis of deuteroacetylene. Hydrogen atoms were not observed in the acetylene–argon photolytic system, suggesting that this photolysis is a second-order process involving two molecules of acetylene. Vinyl radical was obtained by the addition of an H atom, obtained from the photolysis of HI, to acetylene. The ESR spectrum of the vinyl radical consisted of eight broad overlapping lines resulting from the interaction of the unpaired electron with three nonequivalent protons. Addition of an H atom to deuteroacetylene at 4.2°K gave only one of the two possible structural isomers of the 1,2 dideuterovinyl radical. The ESR spectrum of this radical showed that the largest of the proton hyperfine splittings in vinyl is due to a β proton. With the aid of theory the observed hyperfine splittings were assigned to the vinyl protons as follows: $A_{trans,\beta}=68$ Oe, $A_{cis,\beta}=34$ Oe, and $A_{\alpha}=16$ Oe, where the designations *cis* and *trans* refer to the relative positions of the β proton and the unpaired electron orbital. A theoretical treatment of the α proton splitting in vinyl and similar radicals provided a qualitative explanation of the marked difference between the α proton hyperfine splittings in the vinyl and formyl radicals.

I. INTRODUCTION

IN most of the free radicals which have been studied to date the unpaired electron is located, to a zero-order approximation, in $p\pi$ orbitals on one or more atoms of the radical. These radicals, which are called π-electron radicals, have been subjected to extensive experimental and theoretical study, so that a great deal is known about them. Recently, however, studies have been made of several radicals in which the unpaired electron occupies an sp hybrid σ orbital. These radicals, which we call σ-electron radicals, have some novel features not found in π-electron radicals. For example, both the formyl radical[1] (HC=O) and the HPO_2^- radical[2] have been found to have very large proton hyperfine splitting constants.

In this paper we report on the electron spin resonance (ESR) study of two more σ-electron radicals. These are the vinyl radical (HC=CH_2), which is isoelectronic to formyl, and the ethynyl radical (C≡CH). The radicals were studied while trapped in an argon matrix at liquid helium temperatures. Observations of the proton hyperfine splittings in these radicals has yielded some interesting results, and has added to our knowledge of the relation between proton hyperfine splittings and structure in σ-electron radicals.

Many of the σ-electron radicals contain a multiple bond and the photochemical processes used to prepare these radicals are of the following types. (1) Photolytic dissociation of a parent molecule containing the corresponding multiple bond. An example of this is the production of ethynyl by the photolysis of acetylene. (2) The addition reaction of a hydrogen atom, usually obtained by the photolysis of HI, with a molecule containing a multiple bond or a lone pair of electrons. Examples of this reaction are the production of vinyl and formyl[1,3] by the addition of an H atom to acetylene and carbon monoxide, respectively. Experiments of this type not only make free radicals available for ESR study, but the radicals formed and the conditions required for their formation give information about the photochemical reaction employed. A number of especially interesting features have been observed in the photolytic dissociation of acetylene, which illustrate some of the complications which can occur in photochemical reactions of this type.

II. EXPERIMENTAL

The liquid-helium cryostat, sample deposition system, and ESR spectrometer have all been described previously.[4–6] The ethynyl radical was prepared by the photolysis of acetylene using an rf discharge in H_2 gas as the light source. The sample was separated from the discharge by a sapphire window. The concentration of acetylene in the argon matrix was of the order of 0.2 mole %.

The acetylene used in this experiment was Matheson purified grade with a stated purity of 99.5% which was condensed and outgassed at liquid-nitrogen temperature before the vapor sample was taken from the liquid near its freezing point. The results to be dis-

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domly oriented radicals, persuasively demonstrating the power of electron spin resonance spectroscopy.

The second paper reported the electron spin resonance spectra of ethynyl ($HC=\dot{C}$) and vinyl ($H_2\dot{C}=CH$) and also σ radicals. Ethynyl produced a relatively simple narrow line spectrum. Vinyl, however, gave a complex spectrum of eight broad overlapping lines caused by an anisotropic hyperfine interaction (i.e., the magnetic interaction between the electron spin and a nuclear magnetic moment) with three nonequivalent protons. Deuteron substitution for one of the protons permitted one of the proton splittings to be assigned unambiguously. The remaining assignments were then possible with a high degree of certainty from theoretical considerations. The work was of considerable interest in demonstrating the very sensitive effect of structure (i.e., the $H-\dot{C}=CH_2$ bond angle) on the hyperfine interaction with the α proton (i.e., $(H-\dot{C}=)$ in σ radicals.

The experiments described in these articles demonstrated again how careful work on molecular systems that are relatively simple and tractable can lead to a basic understanding of general principles that can be applied to a wide range of more complex systems.

THE HUNT FOR THE ELUSIVE HO_2

SAMUEL N. FONER

S. N. Foner and R. L. Hudson, "Mass Spectrometry of the HO_2 Free Radical," *J. Chem. Phys.* **36,** 2681-2688 (1962).

The paper on "Mass Spectrometry of the HO_2 Free Radical," published in 1962, has an interesting history. The reported work started back in 1953 when Dick Hudson and I published a paper that reported on a very sensitive, novel mass spectrometer that used a collision-free, modulated, molecular-beam sampling system to detect highly reactive species, such as atoms and free radicals, in chemical reactions.[1] The wide applicability of the technique was illustrated by studies of low-pressure hydrogen-oxygen and methane-oxygen flames. Requests for reprints of the paper were exceptionally high, and we had to limit distribution to preserve some copies for ourselves. Shortly thereafter, we reported on the detection of the hitherto elusive HO_2 free radical in the gas-phase reaction of hydrogen atoms with oxygen molecules.[2]

The hydroperoxyl radical (HO_2) is an important chemical intermediate in theories of oxidation, combustion, and explosions; it has been implicated in such diverse phenomena as radiation damage in biological systems and the depletion of the atmospheric ozone layer. Although the existence of the HO_2 free radical was established in the definitive 1953 experiments[2] as a real physical entity rather than as a convenient theoretical construct, the concentration of the radical was inadequate for precise measurements of its thermochemical properties. The experiments had used the classical reaction for HO_2 formation in the hydrogen-oxygen reaction, namely, $H + O_2 + M \rightarrow HO_2 + M$, where M is a third body to carry away excess momentum. An electrical discharge was used to produce the hydrogen atoms. A problem with this approach is that the requirement for a three-body reaction is favored by high pressures, while the yield of hydrogen atoms from an electrical discharge peaks at low pressures. The result was that the concentration of HO_2 attained in the experiments was rather low—about 0.001 percent of the overall gas composition.

To improve the measurement situation and to make studies of this radical accessible to other techniques such as optical spectroscopy, microwave spectroscopy, and electron spin resonance, we investigated a number of alternative ways to generate HO_2 radicals. Instead of synthesizing HO_2 by adding hydrogen atoms to oxygen molecules, we found that various decomposition reactions involving hydrogen peroxide (H_2O_2) were more efficient sources of the HO_2 radical. The simplest and most effective arrangement was to subject a rapidly flowing stream of H_2O_2 vapor to a low-power (barely visible) electrical discharge. What happens here is that the electrical discharge breaks some of the H_2O_2 into OH radicals that react very rapidly with the remaining H_2O_2 molecules in the highly exothermic reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$. The concentration of HO_2 radicals attainable was on the order of 0.3 percent, making it relatively easy to carry out experiments.

The cited 1962 paper presented results on the production, identification, and determination of thermochemical energies of HO_2 radicals. Measurements of the ionization potential of the HO_2 radicals and the $H-O_2$ bond dissociation energy were reported. Estimates were also made of some chemical reaction rates involving HO_2 radicals.

The paper probably attracted wide attention because it provided a comprehensive summary of mass spectrometric work on the HO_2 free radical and its energetics and served as a useful jumping-off point for studies of that important radical by alternative methods. Since this work appeared, the HO_2 free radical has been

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Mass Spectrometry of the HO_2 Free Radical*

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(Received November 29, 1961)

Mass spectrometric studies on the production, identification, and determination of thermochemical energies of HO_2 radicals are reported. Reactions found to produce HO_2 radicals, and examined in some detail, were: (1) reaction of H with O_2, (2) reaction of H with H_2O_2, (3) reaction of O with H_2O_2, (4) reaction of OH with H_2O_2, (5) photolysis of H_2O_2, and (6) low-power electrical discharge in H_2O_2. Of the reactions studied, the low-power electrical discharge in H_2O_2 provided the most intense and convenient source of HO_2 radicals. Ion-molecule reactions, which are negligible in normal operation of our mass spectrometer, are shown to be a potentially serious source of interference in studies of HO_2 with conventional mass spectrometers.

The ionization potential of HO_2, $I(HO)_2$, and the appearance potential of HO_2^+ from H_2O_2, $A(HO_2^+)$, have been redetermined, and the bond dissociation energies D(H—OOH) and D(H—O_2) have been recalculated. The measured values are: $I(HO_2) = 11.53 \pm 0.02$ ev, $A(HO_2^+) = 15.36 \pm 0.05$ ev with an estimated absolute accuracy of ± 0.1 ev. The derived thermochemical energies are: D_0(H—OOH) $= 88.4 \pm 2$ kcal/mole, D_0(H—O_2) $= 45.9 \pm 2$ kcal/mole, $\Delta H_0^0(HO_2) = 5.7 \pm 2$ kcal/mole for the values at 0°K; and D(H—OOH) $= 89.6 \pm 2$ kcal/mole, D(H—O_2) $= 47.1 \pm 2$ kcal/mole, ΔH_{298}^0 (H—O_2) $= 5.0 \pm 2$ kcal/mole for the corresponding values at 25°C. Possible sources of error are examined and their effect on these values is discussed.

I. INTRODUCTION

THE HO_2 radical is an important intermediate in theories of oxidation, combustion, and explosion processes. The existence of HO_2 was apparently first suggested by Marshall[1] in order to explain the formation of hydrogen peroxide by uv irradiation of a mixture of hydrogen and oxygen. Indirect evidence for the participation of HO_2 in reactions is rather extensive. The thermal reaction of hydrogen and oxygen[2] probably provides the strongest indirect evidence for HO_2 in a gas-phase reaction. In this reaction, HO_2 is necessary as a radical chain breaking species to explain the second explosion limit.

Direct experimental proof of the existence of HO_2 was obtained by Foner and Hudson[3] in a mass spectrometric study of the reaction of hydrogen atoms with oxygen molecules. Mass spectrometric detection of HO_2 has also been reported by Robertson[4] in the reaction of hydrogen atoms with oxygen, by Ingold and Bryce[5] in reactions of hydrogen and methyl radicals with oxygen, and by Fabian and Bryce[6] in the methane–oxygen reaction. The ionization potential of the HO_2 radical and the H—O_2 bond dissociation energy have been measured.[7]

Because of the general interest in the physical and chemical properties of the HO_2 radical, serious efforts have been made to study the radical by optical spectroscopy, microwave spectroscopy, and electron spin resonance. Although the infrared detection of the HO_2 radical has been reported in absorption[8] and emission,[9] the identifications have not been confirmed by subsequent work.[10] Electron spin resonance studies on (1) electrical discharge products from water and hydrogen peroxide, condensed at liquid nitrogen temperature[11,12] and at liquid helium temperature[13] and (2) products generated by uv irradiation of hydrogen peroxide–water solutions at 77°K[14] and 90°K,[15] consistently show a broad asymmetrical line (with variations in shape depending on experimental conditions) near the free-electron position which is probably due to HO_2 radicals trapped in the solid.

In this paper, mass spectrometric studies are presented on the production, identification, and determination of energies of HO_2 radicals. A number of reactions for generating HO_2 radicals are discussed. Because of its importance to the thermochemistry of

* This work was supported by the Bureau of Naval Weapons, Department of the Navy.

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studied extensively and characterized in the gas phase by microwave spectroscopy, electron spin resonance, and infrared laser magnetic resonance, as well as mass spectrometry, and in low-temperature solid matrices by optical spectroscopy and electron spin resonance.

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PREDICTING THE EFFECT OF THE TRAP ON THE TRAPPED RADICAL

FRANK J. ADRIAN

F. J. Adrian, "Matrix Effects on the Electron Spin Resonance Spectra of Trapped Hydrogen Atoms," *J. Chem. Phys.* **32**, 972-981 (1960).

About 1958, C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers showed that paramagnetic atomic and molecular fragments, known as free radicals, produced in electric discharges and other energetic processes could be trapped in inert gas matrices at liquid helium temperature and then identified and characterized structurally by electron spin resonance spectroscopy.[1] That development not only opened an important field of experimental research that is still being pursued profitably at APL and elsewhere, but also raised a number of challenging theoretical problems.

Of especial interest were the small matrix-dependent deviations of the electronic magnetic moment (electron *g*-factor) and the electron-nuclear hyperfine structure splitting of the trapped hydrogen atom from the free atom values. The matrix shifts were of fundamental interest insofar as they resulted from, and could provide information about, the interatomic interactions between a hydrogen atom and a matrix atom. They also were of practical interest for the hydrogen maser, which uses the hydrogen atom hyperfine structure splitting as a frequency standard, because hyperfine structure shifts resulting from the collision of a gas-phase hydrogen atom with a buffer gas atom or the container walls could limit the accuracy of the maser.

The problem fitted in well both with work done as part of my doctoral thesis at Cornell University and with work then going on at APL on color centers in alkali halides. The former had involved Van der Waals interactions in which two atoms attract each other by correlating their electron motions so that the instantaneous dipole moments of the atoms are in an attractive configuration (i.e., $(+\ -)\ldots(+\ -)$, where $+$ denotes the atomic nucleus and $-$ its electron charge cloud), more often than they are in a repulsive $(+\ -)\ldots(-\ +)$ configuration. It turned out that the interaction tends to expand slightly the electron charge cloud of the hydrogen atom, thereby increasing the Van der Waals attraction by increasing the magnitude of the instantaneous atomic dipole moments. This decreases both the electron charge density at the hydrogen atom nucleus and the hyperfine structure splitting that is proportional to that quantity.

The color center work, on the other hand, had involved the effects of a shorter range repulsive interaction that arises when the electron charge cloud of a paramagnetic species (such as an electron trapped at a vacancy in an ionic crystal or the present hydrogen atom) overlaps the closed-shell electron cloud of an ion or an inert gas atom. The interaction, which is a consequence of the Pauli exclusion principle that forbids two electrons of the same spin from occupying the same spatial region, shrinks the hydrogen electronic charge cloud slightly to reduce the forbidden overlap. This increases the electron density at the hydrogen atom nucleus and increases the hyperfine structure splitting, just the opposite of the Van der Waals interaction.

The electronic *g*-factor shift was another consequence of the repulsive interactions, specifically the quantum mechanical admixture of small amounts of the electronic orbitals of the matrix atom into the hydrogen atom orbital; this also reduces the forbidden overlap if the signs of the mixing coefficients are chosen properly. The resulting orbital motion of the hydrogen atom electron in the unsymmetrical (*p* state) inert gas orbitals yielded a small orbital magnetic moment that combined with the pure spin moment to give a net moment different from the free-atom value.

The model agreed both qualitatively and quantitatively with experimental observations.[2] For example, hydrogen atoms trapped in cramped interstitial sites of the inert gas matrices where the short-range repulsive interactions were dominant had sizable *g* shifts and positive hyperfine structure shifts, whereas hydrogen atoms trapped in relatively open substitutional sites where the longer range Van der Waals interactions were dominant had very small *g* shifts and negative hyperfine structure shifts. It is also believed that these results were comforting to the developers of the hydrogen maser because not only were the matrix hyperfine structure shifts small but it was likely that wall coatings could be found that would cancel the positive and negative contributions to

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Matrix Effects on the Electron Spin Resonance Spectra of Trapped Hydrogen Atoms*

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A study is made of the matrix effects on the electron spin resonance (ESR) spectra of hydrogen atoms stabilized in nonpolar matrices. It is assumed that the perturbing effect of the matrix consists of van der Waals interactions and the overlap or Pauli exclusion forces. These two effects are treated separately and the results added to get the net result. The van der Waals effect, which is treated by perturbation theory, leads to a reduction in the hfs splitting. The overlap effect, which is treated by requiring that the hydrogen atom wave function be orthogonal to the wave functions of the matrix particles, leads to an increase in the hfs splitting. In addition, the exclusion effect tends to introduce a small amount of the unpaired electron charge density onto the matrix particles. This can lead to a change in the electronic g factor, and also to hyperfine interactions with the nuclei of the matrix particles. The theory gives a good qualitative picture of the various matrix effects and their dependence on various properties of the matrix atoms and molecules.

I. INTRODUCTION

ELECTRON spin resonance (ESR) studies of atoms and free radicals trapped at low temperatures in various inert matrices show that the matrix fields perturb the trapped species.[1,2] In most cases studied to date the matrix perturbations have been quite small (weak matrix field), although easily discernable by the high resolution ESR experiments. In such cases, the trapped atom or radical is almost but not quite free, and the main features of the ESR spectrum pertain to the isolated radical, while the finer details are due to the interaction between the trapped radical and its environment.

Larger matrix effects are quite possible in matrices composed of polar molecules such as H_2O (strong matrix field), or in those cases where the ground state of the trapped paramagnetic species is degenerate, e.g., Cl and NO. Unfortunately, the experiments aimed at studying cases of this type have been rather unsuccessful,[1] most likely because the large matrix perturbations are sufficiently anisotropic to produce severe line broadening in a polycrystalline sample. It is quite likely that such experiments will have to be conducted in single crystal samples, a rather formidable complication. The strong matrix field case is probably best treated by some modification of crystal field theory. An example of this method is the work of Herzfeld[3] on the optical spectra of N atoms trapped in molecular nitrogen. However, because of the scarcity of ESR data on radicals trapped in polar matrices, we shall limit the present study to matrices such as molecular hydrogen and the monatomic gases where one can expect weak matrix fields.

The presence of an interaction between the trapped paramagnetic species and the matrix is quite expected. The matrix perturbation can, however, affect the ESR spectrum in a surprisingly large number of ways, and these various effects can combine to produce rather puzzling spectra. The following is a partial list of phenomena which can be caused by matrix effects[4]:

1. Shifts in the hyperfine structure (we abbreviate this term as hfs) splitting constants. These arise because the matrix perturbs slightly the unpaired electron density at the nuclei of the paramagnetic species. For H atoms trapped in H_2, and in various monatomic gases these shifts are roughly 0.5 to 1.0% of the free atom value. Both positive and negative shifts have been observed.[2]

2. Shift in the spectroscopic splitting factor or g factor g_J. This effect is due to the spin-orbit interaction of the unpaired electron in the field of the matrix particles.[2]

3. Multiple lines can arise if there are different trapping sites within a matrix which produce different shifts in the hfs constants, and/or in g_J.[2]

4. Hyperfine interactions with magnetic nuclei belonging to the matrix particles. Such interactions produce additional lines in the ESR spectrum.[2a]

In this paper we shall present a semiquantitative discussion of the above phenomena for the case of H atoms trapped in molecular hydrogen and in various monatomic gas matrices. Similar considerations will apply to more complicated radicals trapped in such matrices, although numerical estimates will be more difficult to obtain. This limitation is of secondary importance, since the present model is rather crude, even for the simplest case of trapped H atoms, and must be regarded as a qualitative rather than a quantitative theory. The goal of the present study is to show that interactions between the trapped H atom and the

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[1] Jen, Foner, Cochran, and Bowers, Phys. Rev. **112**, 1169 (1958).

[2] (a) Foner, Cochran, Bowers, and Jen, J. Chem. Phys. **32**, 963 (1960); (b) Cochran, Bowers, Foner, and Jen, Phys. Rev. Letters **2**, 43 (1959).

[3] C. M. Herzfeld, Phys. Rev. **107**, 1239 (1957).

[4] An additional effect is the presence of satelite lines which occur when the electron spin transition is accompanied by a nuclear spin flip. This effect was first observed by Zeldes and Livingston, Phys. Rev. **96**, 1702 (1954), and the theory was developed by Trammell, Zeldes, and Livingston, *ibid.* **110**, 630 (1958).

the hyperfine structure shifts. In any event, there was considerable interest in the paper because its methods and results were applicable to a variety of problems involving paramagnetic atoms in solids and gases and paramagnetic defects, color centers, etc., in solids.

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