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The objective of this research was the characterization of molecular species which are important because of (a) their occurrence in high-temperature environments, as for example in the vapor over refractory solids, and in combustion, flames, and propellant burning; (b) their relevance to clarification and/or extension of the basic theory of molecular properties. The molecules studied were usually highly reactive or metastable and often inaccessible by the usual gas-phase spectroscopic methods. They were therefore trapped in a solid (continued)			

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cont. matrix, usually neon or argon, at 4° K and investigated by optical and electron-spin-resonance (ESR) spectroscopies. This isolation procedure is known to produce only small perturbations and to yield information pertinent to the gas-phase species. The species studied included boron and bromine atoms, methylene radicals, diatomic boron, beryllium hydroxide, diatomic chlorine anion, carbonyl silene, diazasilene, the first-row transition-metal mono-, di-, and tri-fluorides and their corresponding hydrides and oxides, and a few rare-earth hydrides and fluorides. Vibrational frequencies, electronic transitions, g factors, spin-rotation constants, hyperfine coupling constants, zero-field-splittings, ground-state multiplicities, and perhaps some information about structure, were obtained. The molecules contained from one to seven unpaired electrons.

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8. PUBLICATIONS:

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## 9. RESEARCH OBJECTIVES

1. Characterization of molecular species which are important because of
  - (a) their occurrence in high-temperature environments, as for example in the vapor over refractory solids, and in combustion, flames, and propellant burning.
  - (b) their relevance to clarification and/or extension of the basic theory of molecular properties.

Such species are usually highly reactive and often inaccessible for study by the usual gas phase methods.

2. Exploitation of the matrix-isolation technique to allow the experimental investigation of molecules that are presently impossible or very difficult to study spectroscopically in the gas phase, particularly via electron-spin-resonance (ESR). In this technique the vapor species are trapped in solid neon or argon on a transparent window or dielectric surface at 4°K. The essential virtues of this procedure are (i) the long lifetime of the metastable species in such an inert rigid environment and at such a low temperature, and (ii) the population of only the zero-point vibrational level of the ground electron state of the molecule at 4°K.

## 10. ACCOMPLISHMENTS

Optical and ESR spectroscopy, and theory, have been applied to characterize a wide variety of small molecules meeting the above criteria. Generally these are the hydride, fluoride, and oxide molecules of the transition and rare-earth metals (usually of high spin), but radicals such as CH<sub>2</sub>, BeOH, B<sub>2</sub>, and SiCO have also been studied. Abstracts of most of the papers dealing with these molecules are given on the next few pages.

## B atoms, B<sub>2</sub> and H<sub>2</sub>BO molecules: ESR and optical spectra at 4°K\*

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(Received 3 March 1976)

Elemental boron has been vaporized and trapped in solid argon at 4-10°K. The Douglas Herzberg transition of B<sub>2</sub> has been observed in absorption at 3300 Å at 10°K, indicating that the lower  $\Sigma$  state is the ground electronic state. However, B<sub>2</sub> was not observed via ESR, which is interpreted as support for a  ${}^2\Sigma_g$  ground state with a zero-field splitting greater than about 4 cm<sup>-1</sup>, rather than  ${}^2\Sigma_u$  favored by *ab initio* calculations. The ESR spectrum of B atoms in solid argon is also detected. It exhibits axial symmetry and almost complete quenching of the orbital angular momentum of the  ${}^2P_{1/2}$  free atom, with  $g_{||} = 2.0014(5)$ ,  $g_{\perp} = 1.9645(30)$ . The simple crystal field model has been applied in the interpretation of the  $g$  and hyperfine tensors and comparison made with Al and Ga in argon, as studied by Ammeter and Schlosnagle. The ESR spectrum of H<sub>2</sub>BO, appearing as an impurity, was observed for the first time, and its magnetic parameters determined.

## ESR of $\text{Cl}_2^-$ in various ion pairs at 4 °K and the theory of V centers

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ESR spectra have been measured of  $\text{M}^+\text{Cl}_2^-$  ion pairs trapped in solid argon at 4°K, where  $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Li}, \text{Na}, \text{and K}$ . The derived  $g$  and hyperfine tensors of  $\text{Cl}_2^-$  are interpreted using the simple crystal field model of Schoemaker, and the spin densities and crystal field parameters  $E_i$  are compared with those for V centers in alkali halide crystals. From matrix data, it is proposed that the isotropic hyperfine coupling parameter  $A_{\text{Cl}}$  for interaction with "Cl in pseudo-free"  $\text{Cl}_2^-$  be taken as  $37 \pm 1 \text{ G}$ . A discussion is given pointing out an approximate linear correlation between the nearest interaction distance ( $d$ ) and  $\Delta g_i$  (or  $A_{\text{Cl}}$ ) among all the  $V_k$  centers. Constraints imposed by lattices of varying  $\text{M}^+/\text{Cl}_2^-$  radius ratios cause variations in  $d$  and in the  $s/p$  character in the antibonding  $\text{Cl}_2^-$  electron, leading to corresponding changes in  $A_{\text{Cl}}$  and inverse changes in  $\Delta g_i$ . V centers, with minimum constraints, have maximum values of  $A_{\text{Cl}}$ .

## $\text{SiCO}$ , $\text{SiN}_2$ , and $\text{Si}(\text{CO})_2$ Molecules: Electron Spin Resonance and Optical Spectra at 4 K

R. R. Lembke, R. F. Ferante, and W. Weltner, Jr.\*†

*Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. Received August 2, 1976*

**Abstract:** The  $^3\Sigma$  molecules carbonylsilene,  $\text{SiCO}$ , and diazasilene,  $\text{SiNN}$ , have been prepared by the vaporization and reaction of silicon atoms with  $\text{N}_2$  or  $\text{CO}$  and trapped in various matrices at 4 K. Some or all sites in some matrices induced slight bending of the molecules. Isotopic substitution of  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^{15}\text{N}$ , and  $^{29}\text{Si}$  was employed to obtain hyperfine coupling data in the ESR and shifts in the optical spectra. In solid neon, assuming  $g_{\parallel} = g_{\perp} = g_{\text{Cl}}$ ,  $D = 2.28$  and  $2.33 \text{ cm}^{-1}$  for  $\text{SiN}_2$  and  $\text{SiCO}$ , respectively. Hyperfine splittings confirm the CNDO calculated results which indicate that in both molecules the electron spins are largely in the  $p\pi$  orbitals of Si. Optical transitions with vibrational progressions were observed beginning at 3680 and 3108 Å for  $\text{SiN}_2$  and at 4156 Å for  $\text{SiCO}$ . IR spectra were obtained and stretching force constants calculated. An attempt was made to correlate these vibrational and electronic data with those for  $\text{CCO}$  and  $\text{CNN}$ . Annealing an argon matrix containing  $\text{SiCO}$  to 35 K led to the observation in the IR of  $^1\Sigma \text{Si}(\text{CO})_2$ , a silicon counterpart of carbon suboxide. A corresponding treatment of a  $\text{SiN}_2$  matrix did not produce the  $\text{N}_2\text{SiN}_2$  molecule, nor was the  $\text{N}_2\text{SiCO}$  molecule observed when both ligands were present.

## $\text{TiF}_2$ and $\text{TiF}_3$ Molecules: Electron Spin Resonance Spectra in Rare-Gas Matrices at 4 K

T. C. DeVore and W. Weltner, Jr.\*

*Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. Received February 7, 1977*

**Abstract:**  $\text{TiF}_2$  and  $\text{TiF}_3$  molecules, produced by the vaporization of solid  $\text{TiF}_3$  or a mixture of titanium and a solid fluoride, were trapped in neon and argon matrices at 4–10 K. ESR spectra indicated that  $\text{TiF}_2$  has a trigonal axis of symmetry with  $g_{\perp} = 1.8910(2)$  and  $g_{\parallel} = 1.9912(2)$  and hyperfine tensor components  $A_{\parallel}(F) = -197.9(2)$ ,  $A_{\perp}(F) = -178.2(2)$ ,  $[A(F)] = 47.9(2)$ , and  $[A(F)] = 11.5(2) \text{ MHz}$  (in solid neon). It was concluded that  $\text{TiF}_2$  has a  $^3A_1'$  ground state with the odd electron in a hybridized  $4s$  and  $3d$   $\text{Ti}^{3+}$  orbital perpendicular to the planar ( $D_{3h}$ ) molecule. The excited  $^1E'$  state lies  $\sim 2000 \text{ cm}^{-1}$  higher. The ESR spectrum of  $\text{TiF}_3$  was that of a nonlinear triplet molecule. Its magnetic parameters are  $g_{\parallel} = 1.9149(2)$ ,  $g_{\perp} = 1.9229(2)$ , and  $g_z = 1.9880(2)$ , where the  $z$  axis is parallel to the  $F_1-F_2$  direction. The zero-field-splitting parameters are  $[D] = 0.0782(2) \text{ cm}^{-1}$  and  $[E] = 0.0021(1) \text{ cm}^{-1}$ . The lines were broad, and no hyperfine structure was resolved. Theoretical considerations indicate that the ground state is  $^3B_1$  with the unpaired spins occupying essentially nonbonding  $d$  orbitals on titanium.

## YbH and YbD molecules: ESR and optical spectroscopy in argon matrices at 4°K<sup>a)</sup>

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(Received 3 March 1977)

YbH and YbD molecules have been prepared by the reaction of Yb and H(D) atoms during the formation of an argon matrix at 4°K. Yb atom and YbH absorption and emission spectra were observed. The magnetic parameters of YbH were determined from the ESR spectrum of the  $^2\Sigma$  molecules (with Yb nuclear spin  $I = 0$  and  $I = 1/2$ ) to be  $g_{\perp} = 1.9953(4)$ ,  $g_{\parallel} = 1.9402(2)$ ,  $A_{\perp}(H) = 226$  MHz,  $A_{\parallel}(H) = 224$  MHz,  $A_{\perp}[^{171}\text{Yb}(I = 1/2)] = 5266$  MHz,  $A_{\parallel}[^{171}\text{Yb}(I = 1/2)] = 5724$  MHz. The hyperfine parameters indicate that the spin density is less than 20% on the hydrogen and that the bonding is largely  $\text{Yb}^+\text{H}^-$ . By comparison of experimental parameters with calculated Yb and  $\text{Yb}^+$  data it is deduced that the unpaired electron occupies predominately the  $6s\sigma$  orbital on  $\text{Yb}^+$  with smaller contributions of  $6p\sigma$  ( $\text{Yb}^+$ ) and  $1s\sigma$  ( $\text{H}^-$ ).

## ESR spectra of the $\text{MnO}$ , $\text{MnO}_2$ , $\text{MnO}_3$ , and $\text{MnO}_4$ molecules at 4°K<sup>a)</sup>

R. F. Ferrante, J. L. Wilkerson,<sup>b)</sup> W. R. M. Graham,<sup>c)</sup> and W. Weltner, Jr.

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(Received 15 August 1977)

The molecules  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{MnO}_3$ , and  $\text{MnO}_4$  have been prepared by the vaporization and reaction of manganese atoms with  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , or  $\text{O}_3$  and isolated in various inert-gas matrices at 4°K. ESR has been used to determine magnetic parameters which are interpreted in terms of molecular geometry and electronic structure.  $\text{MnO}$  is confirmed to have a  $\sigma\pi^2\delta^2$ ,  $^2\Sigma^+$  ground state with  $g_{\perp} = 1.990(7)$  (assuming  $g_{\perp} = g_{\parallel}$ ) and a zero-field splitting in accord with the gas phase value  $D = 1.52$   $\text{cm}^{-1}$ . Hyperfine splittings due to the  $^{55}\text{Mn}(I = 5/2)$  nucleus are  $A_{\perp} = 176(8)$  and  $A_{\parallel} = 440(11)$  MHz.  $\text{MnO}_2$  is a linear  $^2\Sigma^+$  molecule with probable configuration  $\sigma\delta^2$ ,  $D = 1.13$   $\text{cm}^{-1}$  (assuming  $g_{\perp} = g_{\parallel} = 2.0023$ ),  $A_{\perp} = 353(11)$ ,  $A_{\parallel} = 731(11)$  MHz.  $\text{MnO}_3$  exhibits very large hf splittings,  $A_{\perp} = 1772(3)$  and  $A_{\parallel} = 1532(3)$  MHz indicative of a  $sd_2$  hybrid  $^2A_1$  ground state of  $D_{3h}$  symmetry. The spectrum of  $\text{MnO}_4$  is consistent with a  $C_{3v}$  molecule distorted from a  $^2T_1$  electronic state in tetrahedral symmetry by a static Jahn-Teller effect.  $g$  and  $A$  tensors are slightly anisotropic;  $g_{\parallel} = 2.0108(8)$ ,  $g_{\perp} = 2.0097(8)$ ,  $A_{\parallel} = 252(3)$ ,  $A_{\perp} = 196(3)$  MHz. The electron hole is almost entirely in an oxygen  $\pi$ -bonded orbital with one oxygen atom displaced along its Mn-O bond axis.

## Electron Spin Resonance of the Ytterbium Fluoride Molecule at 4 K

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The electron spin resonance spectrum of the  $\text{YbF}(^2\Sigma^+)$  molecule matrix-isolated in solid argon has been observed at 4 K.  $g$  tensor and hyperfine tensor components have been measured:  $g_{\perp} = 1.9954(5)$ ,  $g_{\parallel} = 1.9975(5)$ ,  $A_{\perp}(F) = 220(2)$  MHz,  $A_{\parallel}(F) = 134(2)$  MHz,  $A_{\parallel}[^{171}\text{Yb}(I = 1/2)] = 7822(5)$  MHz,  $A_{\perp}[^{171}\text{Yb}(I = 1/2)] = 7513(5)$  MHz. The hyperfine splittings indicate that the spin density on fluorine is only about 2%, indicating that the molecule is essentially an ion pair,  $\text{Yb}^+\text{F}^-$ . About 80% of the spin is in a  $\text{Yb}^+$   $6s\sigma$  orbital and the remainder in  $5d\sigma$  and  $6p\sigma$  on the metal ion. From  $\Delta g_{\perp}$ , the spin rotation constant is estimated to be  $+0.0034$   $\text{cm}^{-1}$ .

## High spin molecules: ESR of MnF and MnF<sub>2</sub> at 4°K

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ESR spectra of the MnF and MnF<sub>2</sub> molecules trapped in neon and argon matrices have been observed at 4°K. MnF was found to have a <sup>6</sup>Σ ground state with the following magnetic parameters in solid neon (assuming  $g = 2.002$ ):  $g_x = 1.999(1)$ ,  $D = -0.0107(1) \text{ cm}^{-1}$ ,  $A_1(\text{Mn}) = 490(5)$ ,  $A_2(\text{Mn}) = 418(1)$ ,  $A_1(\text{F}) = 60(1)$ , and  $A_2(\text{F}) = 85(2) \text{ MHz}$ . MnF is then highly ionic with the spin density on each F<sup>-</sup> probably less than about 5%. The Mn<sup>2+</sup> ion exhibits about 60% of the s character of the free ion. MnF<sub>2</sub> is linear with a <sup>6</sup>Σ<sub>g</sub> ground state with magnetic parameters in solid neon (assuming  $g = 2.002$ ):  $g_x = 1.994(5)$ ,  $D = 0.370(3) \text{ cm}^{-1}$ ,  $A_1(\text{Mn}) = 153(6)$ ,  $A_2(\text{Mn}) = 124(1)$ ,  $A_1(\text{F}) = 19(1) \text{ MHz}$ . Comparison of these parameters is made with those obtained earlier from crystalline MnF<sub>2</sub> and similar magnetic crystals.

Proc. Symp. on High Temperature  
Metal Halide Chemistry (Edited by  
D.L. Hildenbrand and D.D.  
Cubiccioiti) Proceedings Vol. 78-1  
pages 187-198 (The Electrochem.  
Soc. Inc., 1978).

### AN INVESTIGATION OF THE FIRST ROW TRANSITION-METAL FLUORIDE MOLECULES USING ESR SPECTROSCOPY

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#### ABSTRACT

The ground state electronic configuration and magnetic parameters have been determined for several first row transition metal mono-, di-, and tri-fluoride molecules from their ESR spectra at 4°K. The molecules studied have high spin electronic configurations with less than 5% of the free electron spin density residing on the fluorine(s), indicative of highly ionic bonding. Theory and experiment have been correlated to establish or predict their ground electronic states and geometries.

## High spin molecules: ESR and optical spectroscopy of MnH (<sup>7</sup>Σ) and MnH<sub>2</sub> (<sup>6</sup>A<sub>1</sub>) at 4°K<sup>a)</sup>

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MnH and MnH<sub>2</sub> molecules, and their deuterated counterparts, have been trapped in argon and neon matrices at 4°K and observed via infrared, visible, and electron-spin-resonance spectroscopy. The data for MnH support the gas-phase <sup>7</sup>Σ ground-state assignment and yield the magnetic parameters:  $A(\text{H}) < 20$ ,  $A_x(\text{Mn}) = 322(6)$ ,  $A_y(\text{Mn}) = 299(2) \text{ MHz}$ ,  $g_x = 2.001(1)$  (assuming  $g_y = g_z$ ),  $D = -0.002(1) \text{ cm}^{-1}$ . The derived MO description is in essential agreement with the *ab initio* calculations of Bagus and Schaefer. Infrared data indicate that MnH<sub>2</sub> is bent at a bond angle of  $117 \pm 3^\circ$ , and stretching force constants are derived. ESR spectra variations with the matrix used and with isotopic substitution indicate motional effects in some matrices. It is concluded that the ground state is <sup>6</sup>A<sub>1</sub> with  $D = 0.20(2) \text{ cm}^{-1}$  and with the probable hyperfine parameters  $A(\text{H}) = 36$ ,  $A_{xy}(\text{Mn}) = 73 \text{ MHz}$ , where *xy* is an average axis perpendicular to the H-H direction. The bent molecule is justified by Walsh-type theory applied to transition-metal dihydrides. There are indications that the MnH<sub>2</sub> molecule may have also been observed.

### THE FeH MOLECULE AT 4 K

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#### ABSTRACT

FeH and FeD molecules have been trapped in solid argon at 4 K. From the observed infrared frequencies, corrected for small solid-state effects, the gas-phase vibrational properties are predicted to be  $\omega_e'' = 1764(10)$  and  $\omega_e x_e'' = 46(5) \text{ cm}^{-1}$ .  $D_0$  is found to be 2.0 eV from the Birge-Sponer approximation, but is more likely near 1.7 eV on the basis of the application of that approximation to other diatomic hydrides. Five weak electronic transitions (suggesting low  $gf$  values) observed in absorption in the 4000-5000 Å region are probably counterparts of the blue and green band systems in the gas-phase laboratory and stellar spectra. The strongest band occurs at 4190 Å, suggesting that the 4288 Å band studied by Heimer be reinvestigated. Failure to observe an ESR spectrum of FeH in the solid is interpreted as support for an orbitally degenerate ground electronic state, in agreement with the theoretically derived  $^6\Delta$  ground state.

*Subject headings:* molecular processes — transition probabilities

## CrH and CrH<sub>2</sub> molecules: ESR and optical spectroscopy at 4°K

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CrH and CrD molecules have been trapped in solid argon at 4°K. Infrared spectra, when the large anharmonicity is accounted for, yield predicted gas phase vibrational parameters in the ground state  $\omega_e = 1615 \text{ cm}^{-1}$  and  $\omega_e x_e = 17 \text{ cm}^{-1}$ . ESR spectra clearly establish that the molecule has a  $^6\Sigma$  ground state with zero-field-splitting  $D_0 = 0.34(1) \text{ cm}^{-1}$  in solid argon and approximate hyperfine coupling constants  $A(H) = 49(5) \text{ MHz}$ ,  $A(^{53}\text{Cr}) = 53(5) \text{ MHz}$ , and  $g_x = g_y = g_z$ . Several "extra lines" (off-principal-axis absorptions) in the ESR support the assignment. CrH<sub>2</sub> (and CrD<sub>2</sub>, CrHD) was observed in the IR spectra and may also have been detected in the ESR, which tentatively suggest a  $S = 2$  molecule with  $D_0 \approx 0.02 \text{ cm}^{-1}$ .

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TRANSITION-METAL MOLECULES AND WALSH'S RULES--RATIONALIZATION  
OF OPTICAL AND ESR DATA

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The electronic and molecular structures of the transition-metal difluoride, dioxide, and dihydride molecules are rationalized or predicted from proposed molecular orbitals and Walsh-type diagrams based upon optical and ESR spectroscopic data.

## ESR of matrix isolated bromine atoms produced in the $H + Br_2$ reaction <sup>a)</sup>

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The products of the  $H(D) + X_2$  reaction, where X is Br, Cl, or F, have been trapped in solid argon at 4°K and observed via ESR. With  $Br_2$  as reactant the observed spectra are attributed to Br atoms electronically quenched in an axial crystal field. The spectra obtained using the other halogens were not clearly attributable to quenched atoms. The ESR of matrix-isolated Br atoms has not been observed previously. [While this paper was being reviewed, H. Muto and L. D. Kispert observed the ESR spectrum of partially quenched Br atoms in  $\alpha$ -irradiated N-bromosuccinimide single crystals [J. Chem. Phys. **72**, 2300 (1980)] but their magnetic properties are similar to those recently observed by Iwasaki, Toriyama, and Muto for I atoms quenched in solid xenon. For Br:  $g = 2.646(1)$ ,  $g = 1.55(1)$ ,  $|A| = 1937(20)$  MHz,  $|A| = 423(10)$  MHz, and  $Q = 100(10)$  MHz. Comparison was made with crude axial crystal field predictions derived using the magnetic parameters of the gas-phase atoms.