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 matrix isolation.
matrix, usually neon or argon, at 40 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.
AFOSR-TR-81-0179

1. TITLE: High Energy Sources and Materials: High-Temperature Molecules and Molecular Energy Storage

2. PRINCIPAL INVESTIGATOR: Professor William Weltner, Jr.
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8. PUBLICATIONS:


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 4K. 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 4K.

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 CH2, BeOH, B2, 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, B2 and H2BO molecules: ESR and optical spectra at 4 K*

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(Received 3 March 1970)

Elemental boron has been vaporized and trapped in solid argon at 4-10 K. The Douglass Herzberg
transition of B has been observed in absorption at 3300 A at 4 K, indicating that the lower Σ state is
the ground electronic state. However, B was not observed via ESR, which is interpreted as support for a
Σ ground state with a zero-field splitting greater than about 4 cm⁻¹, rather than Σ. Labeled by ab initio
calculations. The ESR spectra of B atoms in solid argon is also detected. It exhibits axial symmetry and
almost complete quenching of the orbital angular momentum of the B; free atom with g = 2.0024 (0,3).
g = 1 (0.45). 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 H2BO, appearing as an impurity, was observed for the first time, and its magnetic parameters determined.
ESR of Cl₂⁻ in various ion pairs at 4 °K and the theory of V centers

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(Received 21 July 1976)

ESR spectra have been measured of M⁺Cl⁻ ion pairs trapped in solid argon at 4 °K, where M⁺ = Mg, Ca, Sr, Ba, Li, Na, and K. The derived g and hyperfine tensors of Cl⁻ are interpreted using the simple crystal field model of Schenkmaker, and the spin densities and crystal field parameters E are compared with those for V centers in alkali halide crystals. From matrix data, it is proposed that the isotropic hyperfine coupling parameter A₀ for interaction with "C in pseudo"free" Cl⁻ be taken as 37 ± 1 G. A discussion is given pointing out an approximate linear correlation between the nearest interaction distance (d) and Δg (or A₀) among all the V centers. Constraints imposed by lattices of varying M⁺/Cl⁻ radius ratios cause variations in d and in the Δg, character in the antibonding Cl⁻ electron, leading to corresponding changes in A₀ and inverse changes in Δg. V centers, with minimum constraints, have maximum values of A₀.

SiC₅⁻, SiN₂⁻, and Si(CO)₂ Molecules: Electron Spin Resonance and Optical Spectra at 4 K


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

Abstract: The \( ^{12} \)C molecules carbon disilene, SiCO, and diazaasilene, SNN, have been prepared by the vaporization and reaction of silicon atoms with N₂ or CO and trapped in various matrices at 4 K. Some or all sites in some matrices produced slight bending of the molecules. Isotopic substitution of \(^{13} \)C, \(^{15} \)O, \(^{17} \)N, and \(^{28} \)Si was employed to obtain hyperfine coupling data in the ESR and shifts in the optical spectra. In solid neon, assuming \( g = g' = g'' \), \( D = 2.28 \) and \( 2.33 \) cm⁻¹ for SiN₂⁻ and SiCO, respectively. Hyperfine splittings confirm the CNDO calculated results which indicate that in both molecules the electron spins are largely in the p orbitals of Si. Optical transitions with vibrational progressions were observed beginning at 3600 and 3108 Å for SiN₂⁻ and at 4156 Å for SiCO. IR spectra were obtained and stretching force constants calculated. An attempt was made to correlate these vibrational and electronic data with those for CO and CN⁻. Annealing an argon matrix containing SiCO to 35 K led to the observation in the IR of \( ^{12} \)Si(CO)₂., a silicon counterpart of carbon dioxide. A corresponding treatment of a SNN matrix did not produce the N-SiN₂⁻ molecule, nor was the N-SiCO molecule observed when both ligands were present.

TiF₂ and TiF₃ Molecules: Electron Spin Resonance Spectra in Rare-Gas Matrices at 4 K

T. C. DeVore and W. Weitner, Jr.*

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

Abstract: TiF₂ and TiF₃ molecules, produced by the vaporization of solid TiF₂ or a mixture of titanium and a solid fluoride, were trapped in neon and argon matrices at 4 °K. ESR spectra indicated that TiF₂ has a trigonal planar ground state with \( g = 1.9910(2) \) and \( g' = 1.9915(2) \), with hyperfine tensor components \( D_{111} = -19 \) 79 (2), \( D_{122} = 1782 (2), \( D_{133} = 1789 (2) \), and \( D_{123} = 11.5 (2) \) MHz (in solid neon). It was concluded that TiF₂ has a \(^{12} \)S ground state with the odd electron in a \(^{3d}_y \) orbital perpendicular to the plane of the \( D_{123} \) molecule. The excited \( ^{12} \)P, state lies at \( \approx 300 \) cm⁻¹ higher. The ESR spectrum of TiF₃, which is a nonplanar trigonal molecule, has magnetic parameters \( g = 1.9149 (2), \) \( g' = 1.9229 (2), \) and \( g'' = 1.9850 (2) \), where the z axis is parallel to the \( ^{12} \)P direction. The zero-field splitting parameters are \( D_{111} = 0.0782 (2) \) cm⁻¹ and \( |E| = 0.0121 (1) \) cm⁻¹. The lines were broad, and no hyperfine structure was resolved. Theoretical considerations indicate that the ground state is \(^{3} \)H₂ with the unpaired spin occupying essentially nonbonding \( d_y \) orbitals on titanium.


YbH and YbD molecules: ESR and optical spectroscopy in argon matrices at 4°K

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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 YbH molecule with Yb nuclear spin I = 0 and spin = 1/2. The g tensor was 1.995(4) and A = 226 MHz, A' = 224 MHz, A' = 226 MHz, and A = 224 MHz. The hyperfine parameters indicate that the spin density is less than 20% on the hydrogen and that the bonding is largely Yb-H. By comparison of experimental parameters with calculated Yb and Yb' data it is deduced that the unpaired electron occupies predominately the 6σ orbital on Yb' with smaller contributions of 6σ (Yb') and 1σ (H).

ESR spectra of the MnO, MnO2, MnO3, and MnO4 molecules at 4°K


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(Received 15 August 1977)

The molecules MnO, MnO2, MnO3, and MnO4 have been prepared by the vaporization and reaction of manganese atoms with O, N2, O2, or O3 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. MnO is confirmed to have a σπ5, σ2 ground state with g = 1.908(1) (assumed g = g/2) and a zero-field splitting in accord with the gas phase value D = 1.32 cm−1. Hyperfine splittings due to the Mn(5/2) nucleus are 5/2 = 7.685 MHz and 5/2 = 2.26(5) MHz. MnO3 is a linear σ2 molecule with probable configuration σπ0, 7 = 1.01(5) cm−1 (assuming g = g/2) and 4 = 531(11) MHz. MnO exhibits very large hf splittings A = 172(2) MHz and A' = 152(2) MHz indicative of a 1σ orbit; hybrid A ground state of D3h symmetry. The spectrum of MnO3 is consistent with C3v, molecule distorted from a T state electronic state in trigonal symmetry by a static Jahn-Teller effect. g and A tensors are slightly anisotropic g = 2.01(5), g = 2.09(1), 4 = 252(13), 4 = 199(13) MHz. The electron hole is almost entirely in an oxygen π-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 YbF3(2) molecule matrix-isolated in solid argon has been observed at 4 K. g tensor and hyperfine tensor components have been measured: g1 = 1.905(5), g5 = 1.9975(5), g6 = 2.00(2) MHz. A = 134(2) MHz, A = 582(2) MHz, A = 7513(5) MHz. The hyperfine splittings indicate that the spin density on fluorine is only about 3%, indicating that the molecule is essentially an ion pair Yb+ F−. About 90% of the spin is in a Yb+ 6σ orbital and the remainder in 5σe and 5σt pairs on the metal ion. From Δg, the spin rotation constant is estimated to be +0.0034 cm−1.
High spin molecules: ESR of MnF and MnF$_2$ at 4-K

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(Received 14 November 1977)

ESR spectra of the MnF and MnF$_2$ molecules trapped in neon and argon matrices have been observed at 4-K. MnF was found to have a $^2$I$_2$ ground state with the following magnetic parameters in solid neon (assuming $g = 2.00$): $A_{\text{F}} = 0.0107$ cm$^{-1}$, $A_{\text{Mn}} = 1.999(1)$ cm$^{-1}$, $g_{\text{Mn}} = 4.00(5)$, $g_{\text{F}} = 2.01(1)$. MnF$_2$ has a $^2$I ground state with the spin density on each F probably less than about 5%. The Mn$^+$ ion exhibits about 90% of the $s$ character of the free ion. MnF$_2$ is linear with a $^2$I$\text{g}$ ground state with magnetic parameters in solid neon (assuming $g = 2.00$): $g_{\text{Mn}} = 1.994(5)$, $D = 0.37(3)$ cm$^{-1}$, $A_{\text{Mn}} = 15.3(6)$ cm$^{-1}$, $A_{\text{F}} = 19(1)$ MHz. Correlation of these parameters is made with those obtained earlier from crystalline MnF$_2$ and similar magnetic crystals.

Proc. Symp. on High Temperature

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 monofluorides, difluorides, and trifluorides from their ESR spectra at 4-K. The molecules studied have high spin electronic configurations with less than 2% of the free electron spin density residing on the fluorine(s), indicating 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 ($^7_2$) and MnH$_2$ ($^6A_1$) at 4-K

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(Received 8 April 1978)

MnH and MnH$_2$ molecules, and their deuterated counterparts, have been trapped in neon and argon matrices at 4-K and observed via infrared, visible, and electron-spin-resonance spectroscopy. The data for MnH support the gas-phase 2 ground-state assignment and yield the magnetic parameter $A(\text{H}) = 20$, $A_{\text{Mn}} = 3320$ MHz, $g = 2.001(1)$ (assuming $g_1 = g_2$), $D = -0.002(1)$ cm$^{-1}$. The derived MO description is in essential agreement with the ab initio calculations of Ragan and Schafer. Infrared data indicate that MnH$_2$ is bent at a bond angle of 117° 30', and stretching force constants are derived. ESR spectra variations with the matrix used and with isotopic substitution indicate conformal effects in some matrices. It is concluded that the ground state is $^2I$ with $D = 0.02(2)$ cm$^{-1}$ and with the principal hyperfine parameters $A(\text{H}) = 36$, $A_{\text{Mn}} = 73$ MHz, where the average axis is 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$_2$ molecule may have also been observed.
THE FCH MOLECULE AT 4 K

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Received 1978 November 9; accepted 1979 February 3

ABSTRACT

FCH 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 \( \omega_v = 1764 \) (10) and \( \omega_x x_0 = 46 \) (5) cm\(^{-1}\). \( \Delta H \) 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 \( g_f \) 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 \( ^3 \Delta \) ground state.

Subject headings: molecular processes — transition probabilities

CrH and CrH\(_2\) molecules: ESR and optical spectroscopy at 4°K

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(Received 20 March 1979; accepted 24 May 1979)

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 \( \omega_v = 1615 \) cm\(^{-1}\) and \( \omega_x x_0 = 17 \) cm\(^{-1}\). ESR spectra clearly establish that the molecule has a \(^3 \Sigma \) ground state with zero-field splitting \( D = 0.34(1) \) cm\(^{-1}\) in solid argon and approximate hyperfine coupling constants \( A(Cr) = 49(5) \) MHz, \( A(Cr) = 53(5) \) MHz, and \( g = 2 \). Several "extra lines" (off-principal-axis absorptions) in the ESR support the assignment. CrH\(_2\) (and CrD\(_2\)) was observed in the IR spectra and may also have been detected in the ESR, which tentatively suggest a \( S = 2 \) molecule with \( D(\Sigma) = 0.02 \) cm\(^{-1}\).
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+Br₂ reaction a)

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(Received 31 October 1979; accepted 1 May 1980)

The products of the H(D)+X₂ reaction, where X is Br, Cl, or F, have been trapped in solid argon at 4.2K and observed via ESR. With Br₂ 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. Kiespert observed the ESR spectrum of partially quenched Br atoms in x-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 = 2.048(3), g = 1.55(1), |\alpha| = 1937(20) MHz, |\delta| = 43(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.