

High-Spin Molecules

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Simple molecules containing transition-metal atoms, such as CrH, MnF, MnH₂, VF₂, MnO₂, and FeF₃, typically exhibit high electronic multiplicities. The application of electron spin resonance (ESR) spectroscopy, so widespread and informative in the study of crystals¹ and organic complexes² containing transition metals, has not been possible for these radicals, since they exist only as transient, reactive, intermediates in the vapor phase. However, matrix isolation, i.e., the trapping of molecules in the solid rare gases at low temperatures, has made such ESR studies feasible. A trapped radical is only slightly perturbed in such an environment, as has been convincingly demonstrated by vibrational and electronic spectroscopy³ and earlier ESR investigations⁴ of matrix-isolated molecules.

Ab initio theoretical treatments can be applied to these relatively small molecules and appear to be increasingly capable of coping with the still rather large number of electrons involved.⁵⁻¹⁴ Earlier calculations on TiO,⁵ VO,⁶ ScF,⁷ and, more recently, MnH,⁸ MnO,¹¹ and FeF,¹³ have supported the findings of high-resolution optical spectroscopy¹⁵⁻¹⁷ by providing the wavefunctions and energies of the lowest electronic states. ESR at 4 K can now take an even closer look, via the experimentally determined magnetic parameters and zero field splittings (zfs), at the electron distributions and interactions and, in some cases, at the molecular structures. Zfs arises from spin-spin and spin-orbit interaction and is characterized by the interaction parameters *D* and *E*.

Here we will give an Account of our matrix-isolation ESR studies of these molecules with multiplicities varying from triplet to octet. Triplet molecules have had a great deal of attention so that our brief discussion of theory will begin with the quartet (*S* = 3/2) case. Extension to higher spins is straightforward. Finally we will be concerned with the information that can be obtained from observed (and also from unobserved!) ESR spectra. This includes an attempt to understand the variation of zfs among these molecules and the presentation of evidence for a "Walsh" rule for the geometry of MX₂ molecules.

The matrix preparation procedure involves the vaporization of a metallic compound to produce the gaseous species, which is then quenched with a large excess of argon or neon onto a sapphire rod held at 4 K.⁴ This rod is lowered into the microwave cavity and the ESR

spectroscopy performed in the usual way (see Figure 1). Photolysis of halogen molecules trapped with the metal atoms can also be used to prepare the metal halides. Hydrides are made by vaporizing the pure metal and simultaneously flowing H atoms (produced by passing H₂ over a tungsten tube at 2300 °C) along with the excess rare gas.¹⁸

For such trapped radicals, one obtains a so-called "powder" ESR spectrum which, because it samples all orientations of the randomly oriented species, is usually spread out over a broad range of magnetic field.^{19,20} As will be discussed in more detail below, for an axial molecule often only the more intense "perpendicular" transitions are observed and an analysis is made simply from the positions of those *xy* lines. Perpendicular refers here to an allowed $\Delta M_S = \pm 1$, $\Delta M_L = 0$ transition with $\theta = 90^\circ$, where θ is the angle between the dc magnetic field and the molecular axis (*z* direction).

Triplet (*S* = 1) Molecules

Classic work on these molecules is that of Hutchison and Mangum²¹ on single crystals containing organic molecules excited to the triplet state, the discovery of the $\Delta M_S = 2$ transition by van der Waals and de Groot,²² and the analysis of the spectra of randomly

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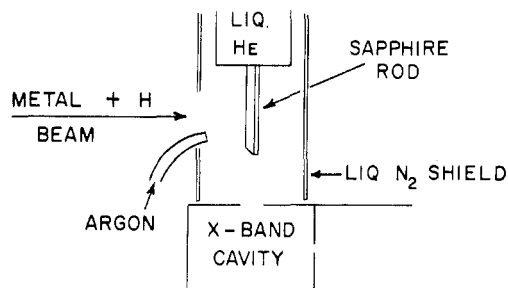


Figure 1. Experimental arrangement for investigating the ESR spectra of matrix-isolated radicals. A metal and hydrogen atom beam was used to form metal hydride radicals.

oriented triplets as expounded by Wasserman, Snyder, and Yager.²³ Since several books^{24,25} and reviews²⁶ have been written on these molecules, mention will be made here only of our ESR results on the TiF_2 molecule,²⁷ which are particularly relevant to later discussion.

In TiF_2 , the titanium atom is bonded to two equivalent fluorine atoms, and the molecule has been shown to be nonlinear from observations of isotopic effects in its matrix IR spectrum.²⁸ This geometry has been supported by its ESR spectrum.²⁷ ESR also reveals that the ground state is 3B with $zfs = |D| = 0.078 \text{ cm}^{-1}$ and $|E| = 0.002 \text{ cm}^{-1}$. The unpaired electrons appear to be confined to the d_{xy} and $d_{x^2-y^2}$ orbitals of the titanium (using the notation for a linear molecule with z axis parallel to the F--F direction), as in a $\text{Ti}^{2+}(3d^2)$ ion. The electrons are so localized that no ^{19}F hyperfine structure (hfs) was observed, which supports the idea of a very ionic molecule.

Quartet ($S = 3/2$) Molecules

The spin Hamiltonian for an $S = 3/2$ molecule, with hyperfine and nuclear Zeeman terms neglected, may be written

$$\mathcal{H} = \beta H g S + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

For the axial case where $E = 0$

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D(S_z^2 - \frac{5}{4}) \quad (2)$$

With the spin basis functions $|+^3/2\rangle$, $|+^1/2\rangle$, $|^-1/2\rangle$, and $|^-3/2\rangle$, the 4×4 eigenvalue matrix from (1) or (2) can be solved exactly for the dc magnetic field along any principal axis.^{29,30} For a linear molecule and H parallel to z

$$W_{\pm 3/2} = D \pm \frac{3}{2}g_{\parallel}\beta H$$

$$W_{\pm 1/2} = -D \pm \frac{1}{2}g_{\parallel}\beta H \quad (3)$$

and the zero-field splitting is then $2D$. Representative Zeeman plots of these energy levels for two values of D (assumed positive) are shown in the right-hand side

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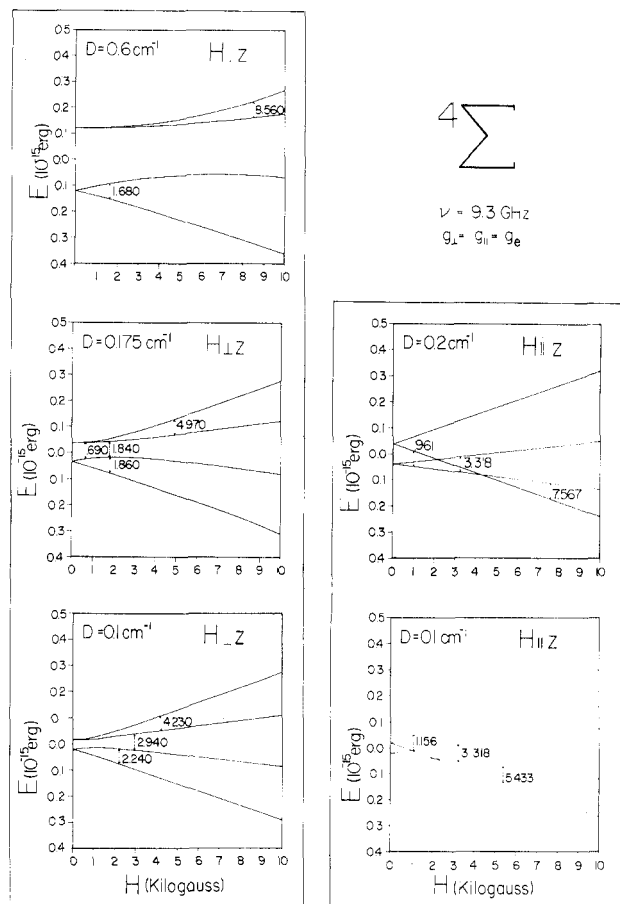


Figure 2. Zeeman levels of a 4Σ molecule for various values of the zero-field-splitting parameter D (assumed positive) and $g_{\perp} = g_{\parallel} = g_e = 2.0023$. The left side of the figure shows E vs. H for the magnetic field perpendicular to the z axis of the molecule ($\theta = 90^\circ$); the right side for H parallel to the axis ($\theta = 0^\circ$). Also shown are the $\Delta M_S = \pm 1$ transitions for each orientation, designated in the text as xy for perpendicular and z for parallel, for $\nu = 9.3 \text{ GHz}$ ($= 0.0616 \times 10^{-15} \text{ erg} = 0.31 \text{ cm}^{-1}$). The energy level spacing at zero magnetic field is $2|D|$.

of Figure 2. For $h\nu = 9.3 \text{ GHz} = 0.31 \text{ cm}^{-1} = 0.0616 \times 10^{-15} \text{ erg}$, the $\Delta M_S = \pm 1$ transitions are also shown. For $H \perp z$

$$W_{\pm 3/2} = \pm \frac{1}{2}g_{\perp}\beta H + [(D \pm \frac{1}{2}g_{\perp}\beta H)^2 + \frac{3}{4}(g_{\perp}\beta H)^2]^{1/2}$$

$$W_{\pm 1/2} = \pm \frac{1}{2}g_{\perp}\beta H - [(D \pm \frac{1}{2}g_{\perp}\beta H)^2 + \frac{3}{4}(g_{\perp}\beta H)^2]^{1/2} \quad (4)$$

Accurate plots of the energy levels for $H \perp z$ for various values of D are shown on the left-hand side of Figure 2. $\Delta M_S = \pm 1$ transitions are also indicated for these perpendicular transitions.

For low D , a matrix-isolated 4Σ molecule might have the ESR absorption spectrum, and its actually observed first derivative, shown in Figure 3. Here g_{\parallel} has been chosen slightly less than g_{\perp} in order to show all six "principal-axis" lines, otherwise xy_2 and z_2 would overlap. The central $M_S = -1/2 \leftrightarrow +1/2$ transition is much stronger than the other transitions, which are spread out over a larger range of magnetic field. This is an important consideration in analysis of the ESR spectra of trapped high spin radicals.

Then if the parallel (z) and perpendicular (xy) transitions for linear molecules with D values varying from 0 to 1.0 cm^{-1} are calculated, the plot shown in Figure 4 may be drawn.³¹ H here then gives the resonant fields

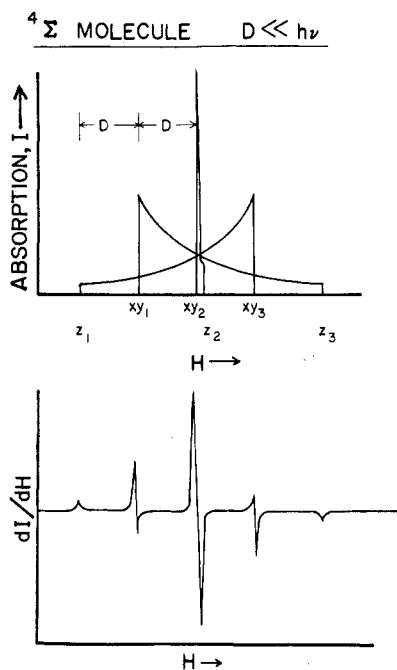


Figure 3. The upper trace indicates the contributions to the absorption spectrum of randomly oriented $^4\Sigma$ molecules with $D \ll g\beta H$. The lower trace indicates the observed ESR spectrum (first derivative of the upper trace). Perpendicular (xy_i) lines dominate, particularly the $M_S = -1/2 \leftrightarrow +1/2$ transition.

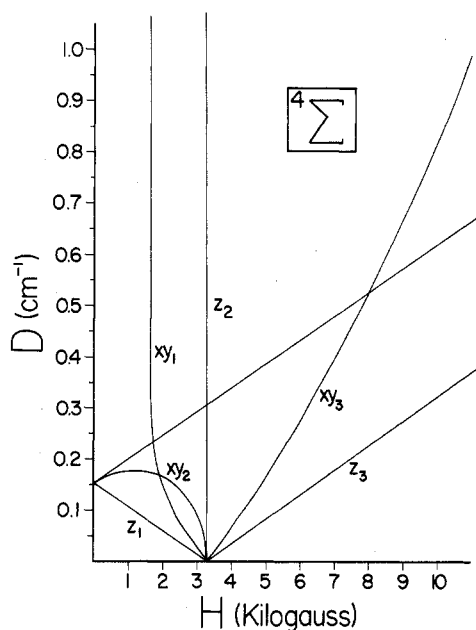


Figure 4. Positions of magnetic fields at which $\Delta M_S = \pm 1$ transitions occur (abscissa) vs. value of the zero-field-splitting parameter D (assumed positive) (ordinate) of a $^4\Sigma$ molecule. It is assumed that $g_{\perp} = g_{\parallel} = g_e$ and $\nu = 9.3$ GHz.

(for $\nu = 9.3$ GHz) at which a molecule with a given D value will have $\Delta M_S = \pm 1$ transitions. The numbering of the parallel and perpendicular transitions in the figure is arbitrarily made from left to right at low D . Thus, as expected, even for very large (positive) D values, the Kramer doublet transitions (xy_1 and z_2) should be observable, but as Figure 3 shows the z transitions are intrinsically weak.

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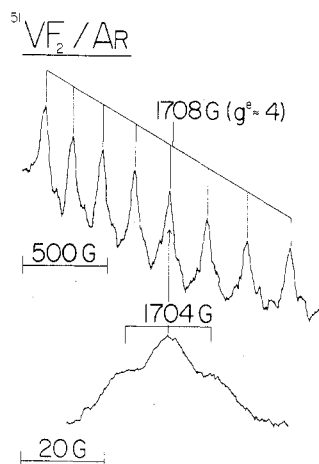


Figure 5. ESR perpendicular (xy_1) line of the VF_2 molecule trapped in solid argon at 4 K. An expanded view of one of the hyperfine structure lines is shown in the lower part of the figure. It exhibits a triplet structure characteristic of two equivalent F atoms. (Reprinted with permission; copyright The Electrochemical Society, Inc. This figure was originally presented at the Fall 1977 Meeting of The Electrochemical Society, Inc., held in Atlanta, GA.)

If D is negative, the energy level schemes in Figure 2 are inverted, but of course the transitions occur at the same fields. However, a lower Boltzmann factor could prevent seeing even the xy_1 and z_2 transitions for large negative D . At 4 K, $D \cong -3.5$ cm^{-1} would cause these transitions to be lowered in intensity by a factor of about 10.

Another way of indicating where a transition lies is to designate its position by an effective g component, g^e . Thus for xy_1

$$g^e_{\perp} \beta H = W_{+1/2} - W_{-1/2} \quad (5)$$

In the limit of high D , this transition appears at an effective $g^e \cong 4$, or more exactly from perturbation theory^{32,33}

$$g^e_{\perp} \cong 2g_{\perp} \left[1 - \frac{3}{16} \left(\frac{g_{\perp} \beta H}{D} \right)^2 \right] \quad (6)$$

for xy_1 . Figure 5 shows this line for the VF_2 molecule where, since ^{51}V has spin $7/2$ and ^{19}F has spin $1/2$, the hyperfine pattern consists of an octet of triplets. The triplet pattern is shown in an expanded view lower in the figure. It seems to exhibit a clear 1:2:1 intensity pattern, compatible with two equivalent F atoms, but undistorted by splitting (into x and y) which would occur if the molecule were bent. $g^e = 3.92$ for this xy_1 line and $|D|$ is then found to be $\cong 0.48$ cm^{-1} , assuming $g_{\perp} = 2.00$. The xy_3 line would appear at the highest fields of our X-band spectrometer, as Figure 4 indicates, and was not observed. Thus, VF_2 is judged to have a $^4\Sigma$ ground state but not to be bent as is its neighbor in the periodic table, TiF_2 .³⁴

MnO_2 is isoelectronic with VF_2 , and its ESR spectrum³⁵ corroborates the findings for VF_2 . A strong

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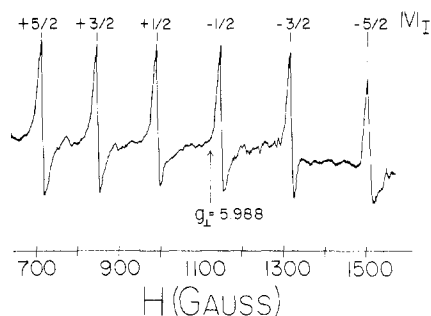


Figure 6. ESR spectrum of the ${}^6\Sigma$ MnO molecule in solid argon at 4 K showing the ${}^{55}\text{Mn}$ hyperfine splitting of the low-field perpendicular (xy_1) line. (Reprinted with permission from *The Journal of Chemical Physics*; copyright American Institute of Physics.)

sextet of lines due to Mn hfs appears at $g^e = 3.990$, and each line has a distinct unsplit perpendicular character, indicating again a ${}^4\Sigma$ molecule. Assuming $g_{\perp} = 2.00$, $|D| \geq 1.13 \text{ cm}^{-1}$ from eq 6.

Earlier ESR work on the diatomics VO^{36} and NbO^{37} established that they are each ${}^4\Sigma$ molecules also, with high D values $\gg 0.3 \text{ cm}^{-1}$. Recent analysis of the VO gas phase optical spectra of Barrow and Richards³⁸ by Veseth³⁹ has yielded $D = 4.11 (3) \text{ cm}^{-1}$, confirming the large zfs.

Other than the lines indicated in Figure 4, because of the extreme variation in absorption with θ in randomly oriented samples, "extra" lines can appear. Such lines were observed for VO and NbO, and for other high-spin molecules. A discussion of their origin is deferred to consideration of $S = 5/2$ molecules.

Quintet ($S = 2$) Molecules

FeF_2 is expected to be of this multiplicity, but attempts to observe its ESR spectrum in matrixes at 4 K were not successful, although FeF_3 ($S = 5/2$)³⁴ could be seen clearly. One explanation of this is that the zfs parameter of FeF_2 is so large that an ESR transition could not be observed at 4 K.

A second possibility, which appears more likely, is that FeF_2 is linear and has an orbitally degenerate ground state, probably ${}^5\Delta$. There is good evidence that it is linear since MnF_2 and CoF_2 are linear according to electric deflection experiments.⁴⁰ As will be explained more fully in a later section, orbital degeneracy leads to a very anisotropic g tensor which would make the spectrum of the randomly oriented molecules unobservable. Reversing this logic, one can say that for linear molecules such "missing" spectra can often be considered as evidence for orbital degeneracy in their ground electronic states.

Our studies, possibly for both of these reasons, have turned up no quintet molecules.

Sextet ($S = 5/2$) Molecules

MnO , MnH_2 , MnF_2 , CrH , and CrF are molecules representative of this multiplicity. A characteristic of

their ESR spectra in matrixes is a strong line at an effective $g^e \cong 6$ (at about 1200 G for X-band), as shown for MnO in Figure 6.³⁵ However, MnF_2 ⁴¹ probably represents a better example of a molecule containing the Mn^{2+} (6S) ion. This ion has been the subject of ESR work in a large number of crystal lattices,¹ usually in an octahedral or slightly perturbed octahedral crystal field. In linear MnF_2 , of course, the "crystal field" would be strictly axial.

In analogy with Figure 4, the variation of the resonant fields at which these transitions occur for molecules with different $|D|$ values can be calculated. At D values greater than 0.2 cm^{-1} the spectrum can be expected to be dominated by two perpendicular transitions; one of these occurs at $g^e \cong 6$ and is relatively insensitive to the exact value of D , as in the ${}^4\Sigma$ case. The additional determination of the position of the second xy_3 transition should, however, indicate unambiguously the magnitude of D . For MnF_2 , for example, both of these xy transitions were observed, and within the error limits set by measurement of the broad xy_3 line, $|D|$ was found to be 0.34 cm^{-1} (assuming $g_{\parallel} = 2.00$) in solid argon.⁴¹ This D value has been confirmed by observation of "extra" lines.

"Extra" lines in powder ESR spectra arise from off-principal-axis absorption, i.e., at θ values other than 0 and 90° , and can lead to considerable complications in the spectra. However, their positions are usually very dependent upon the zfs, so that the additional information obtained from them can make assignments of magnetic parameters more dependable. There has been particular interest in the extra lines observed among the hfs of doublet ${}^{63}\text{Cu}$ molecules.⁴²⁻⁴⁴ Quartet VO^{36} and Cr^{3+} complexes⁴⁵ have also shown extra lines, and the spectra of $S = 5/2$ Fe^{3+} containing molecules have been analyzed⁴⁶ to show that there are many extra lines to be accounted for, particularly at low D values.

Among the high-spin molecules considered here, both MnF_2 and MnH_2 have exhibited off-principal-axis absorptions in the ESR.⁴⁷ These lines are all much weaker than xy_1 and xy_3 , indicating that they may be easily overlooked in other cases if the spectra are not strong.

Septet ($S = 3$) Molecules

The gas-phase optical spectrum of MnH has been thoroughly studied by Nevin and co-workers,¹⁵ and recently Kovács and Pacher have reinterpreted those data.⁴⁸ It was found to be a ${}^7\Sigma$ molecule with a very small zfs, equivalent to $D = -0.002 \text{ cm}^{-1}$. At such low D values one can expect to see predominantly six fine-structure lines in the ESR clustered around $g_{\perp} (\cong g_e$ here), but each of these would be split into 12 hf lines due to electron-nuclear interaction with ${}^1\text{H}$ ($I = 1/2$) and ${}^{55}\text{Mn}$ ($I = 5/2$). Because of the characteristics of

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Table I
High-Spin Molecules

molecule	ground state	$ D $, cm^{-1} ^a	ref
TiF ₂	³ B	0.078	27
VO	⁴ Σ	(+)4.11	36, 38, 39
NbO	⁴ Σ	>>0.3	37
VF ₂	⁴ Σ_{g}	≥ 0.48	34
MnO ₂	⁴ Σ_{g}	≥ 1.13	35
CrF ₃	⁴ A	≥ 0.59	34
CrH	⁶ Σ	0.34	56
CrF	⁶ Σ	0.56	34
MnO	⁶ Σ	(+)2.26	11, 35, 66
MnH ₂	⁶ A	0.26	49
MnF ₂	⁶ Σ_{g}	0.34	41
FeF ₃	⁶ A	≥ 0.84	34
MnH	⁷ Σ	(-)0.002	15, 49
MnF	⁷ Σ	0.011	41
GdF ₃	⁸ A	0.435	53

^a The sign of the zfs parameter is generally undetermined; only for MnH, MnO, and VO is it known. For bent molecules a second parameter, E , should also be given, but is usually unknown, except for TiF₂ where $|E| = 0.002 \text{ cm}^{-1}$.

powder pattern spectra, as indicated earlier for $S = 3/2$ molecules (see also Figure 1, ref 41), there is a severe drop-off in intensity for M_S transitions other than $1 \leftrightarrow 0$ and $0 \leftrightarrow -1$, which are of opposite phase. In fact, only those perpendicular lines are observed for MnH, split by ⁵⁵Mn hf interaction but not by ¹H which is apparently quite small (<20 MHz). The $|D|$ value obtained in solid argon is in exact agreement with the gas-phase value.⁴⁹

MnF is also ⁷ Σ and gives a more striking spectrum in both argon and neon, since the small splitting of 20 G due to ¹⁹F ($I = 1/2$) is observed on each line.⁴¹ The measured $|D| = 0.011 \text{ cm}^{-1}$ is then larger than in MnH.

Octet ($S = 7/2$) Molecules

The Gd atom has a $4f^7 5d^1 6s^2$ configuration, and in the GdF₃ molecule one expects largely ionic bonding of Gd³⁺(4f⁷) with the three F⁻ ions. Electric deflection,⁵⁰ electron diffraction,⁵¹ and IR measurements⁵² support a pyramidal (C_{3v}) structure. The ESR spectrum of matrix-isolated GdF₃ is also most easily interpreted as that of an axial molecule with an octet multiplicity so that its ground state is presumably ⁸A₁.⁵³ Three xy lines were observed along with three weak "extra" lines. A plot of D vs. H for an ⁸ Σ molecule indicates that the observed xy lines fit $|D| = 0.435 \text{ cm}^{-1}$; this was confirmed by fitting the remaining three lines. No fluorine hfs was observed, demonstrating that the molecule is highly ionic. ¹⁵⁵Gd and ¹⁵⁷Gd, each of nuclear spin $I = 3/2$, comprise about 30% of the isotopic natural abundance, and hfs due to these nuclei were observed associated with the strong xy_1 line.

Zero-Field Splitting

The zero-field-splitting parameters for molecules recently observed in our laboratory are given in Table I.

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Spectra were measured only at 4 K so that the signs of the D parameters were not established. For H, F, and O as ligands, theory indicates that generally the electronic states of the diatomic molecules are determined by the properties of the metal atom^{8,11,13} and that, in these ionic diatomics, the metal can be simply characterized as approaching either the +1, +2, or +3 cation. Although the crystal-field model is not considered accurate for prediction of ground states, as attested by the extensive calculations made, for example, on TiO,⁵ VO,⁶ and ScF,^{7,54} we will use it here for a crude correlation of $|D|$ values on the basis of an ionic model for both diatomics and triatomics with varying axial fields produced by the ligands. Accurate theory probably now has the capability of calculating these D values, at least for the diatomics, and considering only the lowest excited states.

D is a traceless tensor, signifying that a spherically symmetric charge distribution will have $D = 0$ (and $E = 0$). (This is true also for a rapidly rotating radical, but ESR evidence excludes rotation of all of these molecules in the matrixes.) A pure d⁵s configuration, like the d⁵s² and d⁵ configurations, is spherically symmetric, and the zfs in the Mn⁺ and Mn²⁺ ions (except for hfs) in a symmetric environment would be expected to be zero or very small.¹ In an axial crystal field the degeneracy of the d orbitals will be split such that three levels now appear, d δ , d π , and d σ . However, if the ligand has only a small axial perturbative effect, as Scott and Richards⁵⁵ have calculated for TiH and VH, then one expects $D \approx 0$. This then appears to be the case for MnH where D is only -0.002 cm^{-1} . Rather surprisingly, substitution of H by F as a ligand leads to only a slight, but measurable, increase in $|D|$, to 0.011 cm^{-1} . However, larger increases are observed in other molecules when H is replaced by F, as seen in Table I.

This simple explanation does not extend to CrH where, on the basis of gas-phase data, Cr⁺ should be a d⁵ ion. Then CrH should also have a small $|D|$ near that of MnH, which is not the case.⁵⁶ Rather, one must assume that the Cr⁺ ion in CrH and CrF has a different configuration, d⁴s, which is a rather low-lying configuration for that ion. Substitution of the fluoride ion does, as in the Mn⁺ case, produce an increase in $|D|$, but here the change is from 0.34 to 0.56 cm^{-1} .

If we may consider the transition metal as an Mn²⁺ ion in the ⁶ Σ molecules MnH₂, MnF₂, and MnO, then it is clear that the oxygen ligand is having a much larger effect than the symmetrically attached H and F ligands. (Recent optical work on MnO⁶⁶ has revised the former D value¹¹ to the higher value given in Table I.) Also, we may note that in spite of a decrease in the number of unpaired spins from MnH to MnH₂ and MnF to MnF₂, there is an increase in D in each case. Thus, despite their symmetrical attachment, additional ligands are producing more distortion of the charge distribution on the Mn ion. The implication is that in MnO₂ $|D|$ should be even larger than the value of 2.26 cm^{-1} found for MnO; however, this is not a straightforward extrapolation since there has been a larger change in multiplicity upon addition of another oxygen ligand than in the hydride and fluoride.

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Information from "Missing" ESR Spectra

There are two reasons for not observing the ESR spectrum of a radical, even if present in high concentration in a matrix: (1) the zfs value may be so large that no transitions occur at X-band frequencies, or (2) the molecule is linear and has orbital angular momentum in the ground electronic state. The first reason is clear, but the second arises because of an extreme anisotropy in the g tensor which may not be so obvious. For example, the principal components of g for a doublet state are $g_{\parallel} = g_e \langle \phi_1 | L_z + 2S_z | \phi_1 \rangle = -g_e \langle \phi_2 | L_z + 2S_z | \phi_2 \rangle$ and $g_{\perp} = g_e \langle \phi_1 | L_x + 2S_x | \phi_2 \rangle$, where L and S are the total orbital and spin angular momentum vectors and $|\phi_1\rangle$ and $|\phi_2\rangle$ are the wave functions of the doublet. If $|\phi_1\rangle = |1, +1/2\rangle$, $|\phi_2\rangle = |-1, -1/2\rangle$ (for $|M_l, M_s\rangle$ with Russell-Saunders coupling), then one finds $g_{\parallel} = 4$, $g_{\perp} = 0$. The latter g component implies a resonance at infinite magnetic field, which in turn implies that the ESR spectrum of these ${}^2\Pi_{3/2}$ randomly oriented molecules will be so spread out as to be unobservable. Then, in general, reason 2 is synonymous with saying that only Σ states of linear molecules will be observed in ESR spectra in matrixes.

The magnitude of $|D|$ among the first-row transition-metal molecules, as seen from Table I, is not expected to be large enough to prevent observation of an X-band ESR spectrum. If we then attribute "missing" spectra to orbital degeneracy in linear radicals, such negative data can serve as another source of information about the ground electronic states of molecules observed in the gas phase. One must, of course, be assured that the molecule of interest is trapped in the matrix.

The following molecules have not been observed via ESR in this laboratory in spite of considerable effort in most cases (the symbols in parentheses indicate what we consider to be the most likely ground electronic state): $\text{FeF}({}^6\Delta)$,^{13,17} $\text{FeH}({}^6\Delta)$,^{10,12} $\text{FeO}({}^5\Delta)$,^{12,57,58} $\text{NiO}({}^3\Pi)$,^{34,58} $\text{CoO}({}^4\Phi)$,^{34,58} $\text{TiH}({}^4\Phi)$,¹² $\text{TiF}({}^4\Phi)$, $\text{TiH}_2({}^3\Phi)$, $\text{FeF}_2({}^5\Delta)$, $\text{NiF}_2({}^3\Pi)$, $\text{CoF}_2({}^4\Delta)$.

The interaction of vibrational and electronic motions in a triatomic linear molecule having a non-zero orbital angular momentum (Renner-Teller effect) may lead to stabilization of a bent molecule.⁵⁹ In such a case, the above listed molecules would be expected to exhibit matrix ESR spectra. Then the fact that such spectra were not observed even at 4 K also implies that such vibronic effects are quite small in these molecules.

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Table II
Configurations and Ground States of
Transition Metal Difluorides and Dioxides

valence electrons		configuration	ground state	difluoride	dioxide
15	bent	b_1''	2B_1		ScO_2
16		b_1''	1A_1		TiO_2
17		b_1''	2B_1	ScF_2	VO_2
18		$a_1' b_1''$	3B_1	TiF_2	CrO_2
19	linear	$\sigma\pi^2$	${}^4\Sigma_g$	VF_2	MnO_2
20		$\sigma\pi\delta^2$	${}^5\Pi_g$	CrF_2	FeO_2
21		$\sigma\pi^2\delta^2$	${}^6\Sigma_g$	MnF_2	CoO_2
22		$\sigma\delta^3\pi^2$	${}^5\Delta_g$	FeF_2	NiO_2
23		$\sigma^2\delta^3\pi^2$	${}^4\Delta_g$	CoF_2	CuO_2
24		$\sigma\delta^4\pi^3$	${}^3\Pi_g$	NiF_2	
25		$\sigma\delta^4\pi^4$	${}^2\Sigma_g$	CuF_2	

"Walsh Rules" for Transition-Metal Triatomics

By simple molecular orbital theory Walsh⁶⁰ rationalized the abrupt change from linear to bent geometry of light triatomics, such as CO_2 , N_2O , and NO_2 , in going from 16 to 17 valence electrons. It appears that an analogous but opposite change occurs among the transition-metal dihalides and dioxides upon the addition of the 19th valence electron.^{34,4,61} Thus although TiF_2 (18 electrons) is bent, ESR and other evidence³⁴ indicates that VF_2 , MnF_2 , and CuF_2 ⁶² are linear. Table II gives our depiction of the most probable structures and ground states of these triatomics containing a first-row transition metal. NiF_2 is probably the most controversial since there are experimental and theoretical results which disagree.³⁴ It is possible that there are closely lying electronic states and thereby fluctuations in structure from FeF_2 to NiF_2 , but lacking supporting experimental evidence, it seems most likely that linearity extends throughout the series after TiF_2 . There is good evidence that TaO_2 ,⁶³ MoO_2 ,⁶⁴ and WO_2 ,⁶⁵ "isoelectronic" with VO_2 and CrO_2 , are bent, which supports and extends these conclusions. One can draw crude Walsh-type energy vs. angle diagrams and rationalize these predictions.⁴

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