

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

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Abstract: TiF₂ and TiF₃ molecules, produced by the vaporization of solid TiF₃ or a mixture of titanium and a solid fluoride, were trapped in neon and argon matrices at 4–10 K. ESR spectra indicated that TiF₃ has a trigonal axis of symmetry with $g_{\perp} = 1.8910$ (2) and $g_{\parallel} = 1.9912$ (2) and hyperfine tensor components $A_{\parallel}(\text{Ti}) = -197.9$ (2), $A_{\perp}(\text{Ti}) = -178.2$ (2), $|A_{\parallel}(\text{F})| = 47.9$ (2), and $|A_{\perp}(\text{F})| = 11.5$ (2) MHz (in solid neon). It was concluded that TiF₃ has a ²A₁' ground state with the odd electron in a hybridized 4s and 3d₂ Ti³⁺ orbital perpendicular to the planar (*D*_{3h}) molecule. The excited ²E'' state lies ~2000 cm⁻¹ higher. The ESR spectrum of TiF₂ was that of a nonlinear triplet molecule. Its magnetic parameters are $g_x = 1.9149$ (2), $g_y = 1.9229$ (2), and $g_z = 1.9880$ (2), where the z axis is parallel to the F–F direction. The zero-field-splitting parameters are $|D| = 0.0782$ (2) cm⁻¹ and $|E| = 0.0021$ (1) cm⁻¹. The lines were broad, and no hyperfine structure was resolved. Theoretical considerations indicate that the ground state is ³B₁ with the unpaired spins occupying essentially nonbonding d orbitals on titanium.

TiF₂ and TiF₃ molecules trapped in solid neon and argon matrices have been observed in the infrared by Hastie et al.¹ Titanium isotope structure was resolved which indicated that TiF₂ is bent at an angle of $130 \pm 5^\circ$. The IR did not establish whether TiF₃ is planar (*D*_{3h}) or pyramidal (*C*_{3v}), however.

TiF₂ and TiF₃ are both of interest electronically. From simple theory the TiF₃ molecule is expected to have one unpaired electron occupying an orbital on Ti along the C₃ axis in the molecule. Because it is also expected to be highly ionic, its properties are then somewhat analogous to those of the Ti³⁺ ion as observed in crystalline environments and molecular complexes. The multiplicity of the ground state of TiF₂ should be a singlet or triplet, but it is not obvious which is correct. The ESR work described here shows definitely that the lowest state is a triplet and also proves conclusively that TiF₂ is a bent molecule.

Experimental Section

The Dewar, furnace assembly, and ESR apparatus used in this study have been described in detail previously.^{2,3} TiF₃ vapor was produced either by heating solid TiF₃ (Apache Chemicals) or a mixture of powdered Ti (Spex) and ZnF₂ (A. D. Mackay, Inc.) to ~700 °C in a resistively heated Ta cell. TiF₂ molecules were present in the vapor over the mixture but at a lower concentration than TiF₃ molecules. They were also produced at low concentration by the vaporization of a mixture of Ti and TiF₃ at ~1300 °C from a Ta cell. The vapor species were then codeposited with argon (Linde) or neon (Linde) on a liquid helium cooled sapphire rod at 4 K for 1 h. The rare gas flow (12–18 mmol/h) used is estimated to produce M/R ratios greater than 500.

ESR Spectra. There are five naturally occurring isotopes of Ti: ⁴⁶Ti (7.93%), ⁴⁷Ti (7.28%), ⁴⁸Ti (73.94%), ⁴⁹Ti (5.51%), and ⁵⁰Ti (5.34%). Two of these isotopes ⁴⁷Ti ($I = \frac{5}{2}$) and ⁴⁹Ti ($I = \frac{7}{2}$) possess nuclear magnetic moments. Hence, if all hyperfine (hf) lines could be observed, the ESR spectrum for a species containing one Ti atom would consist of a strong central line flanked by a much weaker sextet ($I = \frac{5}{2}$) and octet ($I = \frac{7}{2}$). However, since the gyromagnetic ratio is nearly the same for both isotopes ($\gamma = -0.3148$ for ⁴⁷Ti and -0.3149 for ⁴⁹Ti) the patterns are superimposed producing a series of lines with approximate relative intensities 1:3:3:3:120:3:3:3:1.

TiF₃. The ESR spectrum of TiF₃ in an argon matrix is shown in Figure 1. The spectrum of ⁴⁸TiF₃ can be identified by the set of four strong parallel lines near $g = 2.0$ ($H \approx 3350$ G) with relative intensity 1:3:3:1, indicating the presence of three equivalent fluorine nuclei ($I = \frac{1}{2}$) in the molecule. Split out from this pattern are the weaker quartets arising from the other Ti isotopes. The corresponding perpendicular lines are centered about ~3570 G and exhibit a much smaller fluorine hfs.

The spectrum of TiF₃ in neon, shown in Figures 2 and 3, is in general very similar to that observed in argon. The enlarged ⁴⁸Ti bands

are traced in Figure 3. Although the parallel lines clearly exhibit the expected pattern, the perpendicular lines consist of several overlapping lines. (There also may be some distortion among the perpendicular lines in argon, but it is relatively small compared to neon.) These extra lines are believed to arise from at least two sites, a and b, in the neon lattice. Although a ^{47,49}Ti line should lie at the higher field b site position, its intensity is not expected to be nearly as strong as that observed. This perpendicular line pattern could also indicate two *g*-tensor components, implying a nonaxial molecule. In view of the clear 1:3:3:1 pattern of the parallel lines and the smaller distortion of the perpendicular lines in argon this seems unlikely. Another similar possibility is that the site in neon distorts the molecule slightly leading to non-equivalent fluorine atoms, which would also produce the additional hyperfine lines.⁴⁻⁶

Since all *A* values are small compared to the applied magnetic field, the usual second-order solution to the axial spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

was used to determine the values of the *A* and *g*-tensor components.⁷ These values are given in Table I. The agreement between the calculated and the observed line positions using these parameters is indicated in Tables II and III.

TiF₂. The observed spectrum of TiF₂ in a neon matrix is shown in Figure 4. With the exception of small shifts in the line positions, the spectrum in argon, which is not shown, is identical with that in neon. This pattern of seven lines is that expected for a nonlinear triplet molecule with a zero-field-splitting parameter less than $h\nu$.⁸ The spin Hamiltonian for such a molecule may be written as

$$\mathcal{H} = g_x\beta H_x S_x + g_y\beta H_y S_y + g_z\beta H_z S_z + D(S_z^2 - \frac{2}{3}) + E(S_x^2 - S_y^2) + \sum(A_x^i I_x^i S_x + A_y^i I_y^i S_y + A_z^i I_z^i S_z) \quad (2)$$

where *D* and *E* are the zero-field-splitting parameters and the remaining symbols have their usual meaning. The superscript *i* denotes the nuclei possessing spin. The solutions for these transitions, ignoring hyperfine interactions, have been derived by Wasserman et al.⁸ These equations were used to compute the *g* tensor, *D*, and *E*, and the results of this calculation are given in Table IV.

Since the spectrum arising from the titanium isotopes possessing nuclear spin was not observed and the fluorine hfs was also not resolved, it was not possible to determine the *A* tensors for TiF₂. However, maximum values for the fluorine hfs based upon the observed line widths can be estimated, as will be discussed in the next section. A comparison of the observed line positions and the line positions calculated by using the data in Table IV and ignoring the hyperfine interactions is given in Table V.

Discussion

TiF₃. The isotropic and dipolar hyperfine interaction with a particular nucleus for a molecule with axial symmetry can

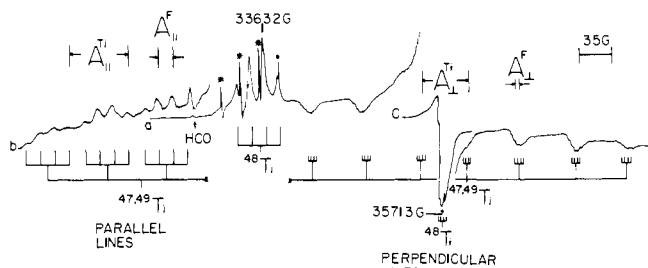


Figure 1. The ESR spectrum of TiF_3 in solid argon at 4 K. The relative gain for spectra 3a:3b:3c is 1:10:0.1, respectively. * indicates CH_3 radicals.

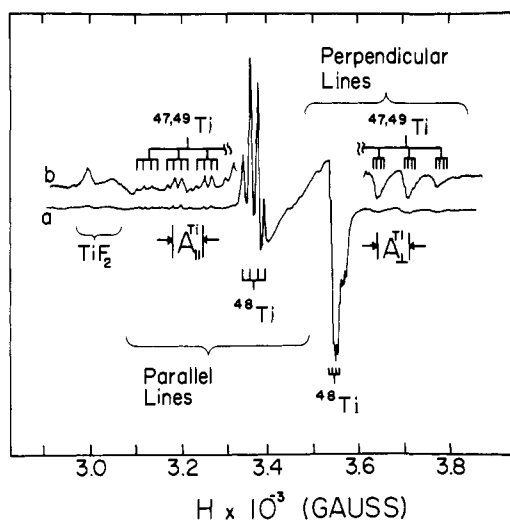


Figure 2. The ESR spectrum of TiF_3 in solid neon at 4 K. Spectrum 2a was measured at one-tenth the gain of spectrum 2b.

be expressed in terms of A_{\parallel} and A_{\perp} as⁹

$$A_{\text{iso}} = \frac{1}{3}(A_{\parallel} + 2A_{\perp}) = \frac{8\pi}{3}g_n\beta_n g_e\beta_e |\psi(0)|^2$$

$$A_{\text{dip}} = \frac{1}{3}(A_{\parallel} - A_{\perp}) = g_n\beta_n g_e\beta_e \left(\frac{3 \cos^2 \theta - 1}{2r^3} \right) \quad (3)$$

The derived values for A_{iso} , A_{dip} , $|\psi(0)|^2$, and $\left(\frac{3 \cos^2 \theta - 1}{r^3} \right)$ for the interaction with the metal and fluorine nuclei in TiF_3 are given in Table I. The signs of the A -tensor components have been assumed to be the same as the nuclear moments. Although this choice seems to be the only meaningful one for the larger Ti splittings, it is not necessarily the case for fluorine. However, regardless of the signs of the fluorine A -tensor components, their magnitudes will be small.

The hyperfine structure requires three equivalent fluorine atoms in TiF_3 . The smallness of these splittings (compared to

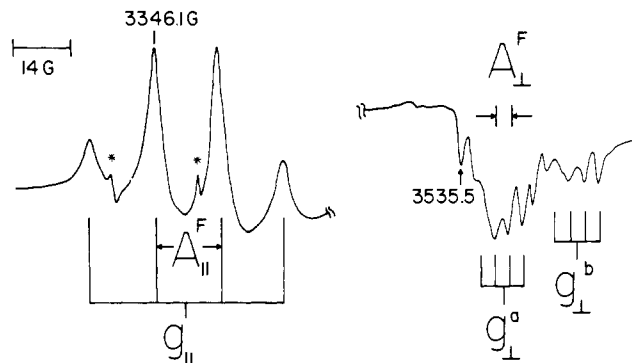


Figure 3. The ESR spectrum of TiF_3 in solid neon at 4 K showing the fluorine hyperfine splitting.

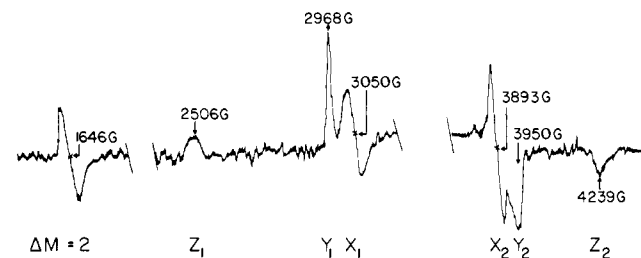


Figure 4. The ESR spectrum of TiF_2 in solid neon at 4 K.

the atomic fluorine values of $A_{\text{iso}} = 47\,910$ MHz and $A_{\text{dip}} = 1515$ MHz¹⁰) clearly indicates that very little spin is on the ligands. Thus the electron is essentially localized in a non-bonding orbital on the titanium. Since the bonds are certainly highly ionic, the titanium can be considered to be a Ti^{3+} ion in a trigonal (most likely planar) field. In this D_{3h} field, the Ti^{3+} ion would have a lowest orbital of a_1' (s , d_{z^2}) symmetry, an orbital higher in energy of e'' (d_{xz} , d_{yz}) symmetry, and a highest level of e' (d_{xy} , $d_{x^2-y^2}$) symmetry. The odd electron is then in an orbital described by an sd_{z^2} hybrid,

$$\psi(a_1') = c_1\chi(3d_{z^2}) + c_2\chi(4s)$$

where the z axis is normal to the plane of the molecule.

The amount of d_{z^2} character, as given by c_1^2 , can be approximated by dividing the value of $A_{\text{dip}}(\text{Ti}) = -6.6$ MHz (in neon, Table I) by -21.9 MHz, which is a theoretical value for a 3d electron on Ti^{3+} ,¹⁰ yielding $c_1^2 \approx 0.30$. Then by difference, one obtains a value of 70% s character for the unpaired electron. This large s contribution is in approximate accord with the large value observed for $A_{\text{iso}}(\text{Ti}) = -185$ MHz. (Use, as above, of the only available atomic value of $A_{\text{iso}} = -492$ MHz, which is for neutral atomic Ti ,¹⁰ yields $c_2^2 \approx 0.38$.)

Table I. Magnetic Parameters for TiF_3 in Neon and Argon Matrices at 4 K

Matrix	g_{\perp}	g_{\parallel}	$A_{\perp}(\text{Ti}),^a$ MHz	$A_{\parallel}(\text{Ti}),^a$ MHz	$ A_{\perp}(\text{F}) ,^a$ MHz	$ A_{\parallel}(\text{F}) ,^a$ MHz	$A_{\text{iso}}(\text{Ti}),$ MHz	$A_{\text{dip}}(\text{Ti}),$ MHz	$ A_{\text{iso}}(\text{F}) ,$ MHz	$ A_{\text{dip}}(\text{F}) ,$ MHz
Neon (site a)	1.8910 (2)	1.9912 (2)								
Neon (site b)	1.8808 (2)	1.9912 (2)	-178.2 (2)	-197.9 (2)	11.5 (2)	47.9 (2)	-184.8 (4)	-6.6 (4)	23.6 (4)	12.1 (4)
Argon	1.8786 (2)	1.9986 (1)	-169.0 (1)	-193.4 (2)	10.3 (2)	44.7 (2)	-177.1 (4)	-8.1 (4)	21.8 (4)	11.5 (4)
			$ \Psi(0) ^2(\text{Ti}), \text{au}$		$ \Psi(0) ^2(\text{F}), \text{au}$		$\langle(3 \cos^2 \theta - 1)/r^3\rangle_{\text{Ti}}, \text{au}$		$\langle(3 \cos^2 \theta - 1)/r^3\rangle_{\text{F}}, \text{au}$	
Neon (site a)			0.735 (5)		0.005 60 (5)		0.440 (5)		0.0480 (5)	
Neon (site b)										
Argon			0.705 (5)		0.005 15 (5)		0.565 (5)		0.0495 (5)	

^a The signs of the A values are taken as those of the nuclear moments (see text).

Table II. Comparison of the Observed and the Calculated ESR Lines for TiF₃ in Solid Neon at 4 K (Site a Only) (Error = ±0.2 G unless noted) (ν 9.386 GHz)

Isotope	M_1^{Ti}	M_1^{F}	Perpendicular lines		Parallel lines	
			Obsd (G)	Calcd (G)	Obsd (G)	Calcd (G)
⁴⁸ Ti		3/2	3329.2	3329.1	3539.3	3539.6
		1/2	3346.1	3346.2	3544.4	3543.7
		-1/2	3363.2	3363.2	3547.9	3547.8
		-3/2	3380.5	3380.4	3551.9	3551.9
^{47,49} Ti	-7/2	3/2		3315.1	3080.0	3079.6
		1/2	3318 (2)	3319.2	3096.6	3096.7
		-1/2	3321 (2)	3323.3	3113.8	3113.8
		-3/2		3327.4	3331.6	3330.6
	-5/2	3/2		3378.8	3150.8	3151.3
		1/2	3382 (2)	3382.9	3168.9	3169.4
		-1/2	3388 (2)	3387.0	3185.3	3185.5
		-3/2		3391.1	3202.4	3202.6
	-3/2	3/2		3439.6	3219.7	3219.5
		1/2		3443.7	3236.8	3236.5
		-1/2	3347 (2)	3447.8	3253.9	3253.5
		-3/2	3452 (2)	3451.9	3271.0	3271.7
	-1/2	3/2	3501.9	3501.7	3289.4	3289.2
		1/2	3506.2	3505.8	3305.9	3306.3
		-1/2	3510.2	3509.9		3323.4
		-3/2	3514.2	3514.0		3340.5
	1/2	3/2		3565.3		3359.8
		1/2		3569.4		3376.9
		-1/2	3574 (2)	3573.5	3396 (2)	3394.0
		-3/2	3577 (2)	3577.6	3412 (2)	3411.1
	3/2	3/2	3630.6	3630.4	3433 (2)	3431.5
		1/2	3634.4	3634.5	3449 (2)	3448.6
		-1/2	3638.7	3638.6	3466 (2)	3465.7
		-3/2	3643.2	3642.7	3483 (2)	3482.8
5/2	3/2	3696.8	3695.9	3505 (2)	3504.3	
	1/2	3700.9	3700.2	3521 (2)	3521.4	
	-1/2	3705.0	3704.6		3538.5	
	-3/2	3709.1	3707.9		3555.6	
7/2	3/2	3759.5	3760.3		3573.8	
	1/2	3763.4	3764.1	3590.1	3590.9	
	-1/2	3768.0	3768.2	3609.1	3608.0	
	-3/2	3771.7	3772.3	3624 (2)	3625.1	

The second-order expression for $\Delta g_{\perp} = g_{\perp} - g_e$ for a molecule with axial symmetry is given by¹¹

$$\Delta g_{\perp} = -2 \sum_n \frac{\langle n | \xi L_x | 0 \rangle \langle 0 | L_x | n \rangle}{E_n - E_0} \quad (4)$$

where the summation is over all states which can couple with the ${}^2A_1'$ ground state of TiF₃, the ground state is denoted by 0, and ξ is the spin-orbit coupling constant. If only the first term in the summation is considered to make a significant contribution, and the wave function for the first excited state is assumed to be

$$\psi(E'') = \chi(e'') = 2^{-1/2}[\chi(3d_{xz}) + \chi(3d_{yz})]$$

where the ligands are assumed to make negligible contributions, then Δg_{\perp} becomes

$$\Delta g_{\perp} = -(6\lambda_{\text{Ti}}/\Delta E)c_1^2 \quad (5)$$

where $\Delta E = E(e'') - E(a_1')$ and λ_{Ti} is the spin-orbit coupling constant for Ti³⁺. Substituting the experimental value of Δg_{\perp} in neon, the value of $c_1^2 = 0.30$ from the A tensor, and $\lambda(\text{Ti}^{3+}) = 154 \text{ cm}^{-1}$,¹² ΔE is estimated to be 2500 cm^{-1} .

In higher order,¹³ $\Delta g_{\parallel} = -3\lambda^2 c_1^2 / \Delta E^2$ and from $\Delta g_{\parallel} = -0.0111$, ΔE is found to be 1400 cm^{-1} , in reasonable agreement with the value obtained from Δg_{\perp} for these wave functions.

The Ti³⁺ ion has almost always been investigated in crystals or molecular complexes where it is in an octahedral or a nearly octahedral field. In these cases, the unpaired electron has only

Table III. Comparison of the Observed and the Calculated Line Positions for TiF₃ in Solid Argon at 4 K (Error = ±0.2 G Unless Noted) (ν 9.385 GHz)

Isotope	M_1^{Ti}	M_1^{F}	Perpendicular lines		Parallel lines	
			Obsd (G)	Calcd (G)	Obsd (G)	Calcd (G)
⁴⁸ Ti		3/2	3563.7	3564.0	3331.0	3331.3
		1/2	3567.8	3567.7	3347.3	3347.2
		-1/2	3571.3	3575.3	3363.2	3363.2
		-3/2	3575.3	3575.0	3379.2	3379.1
^{47,49} Ti	-7/2	3/2		3350.5	3090 (2)	3088.1
		1/2		3354.4	3105 (2)	3104.1
		-1/2		3358.1	3120.1	3120.0
		-3/2		3361.7	3135.9	3136.0
	-5/2	3/2	3411.1	3411.6	3156.3	3157.6
		1/2	3415.1	3415.2	3173.3	3173.5
		-1/2	3418.6	3418.9	3188.9	3189.5
		-3/2	3422.6	3423.4	3206.6	3205.4
	-3/2	3/2	3468.1	3469.2	3223.3	3224.7
		1/2	3471.1	3472.8	3239.8	3240.6
		-1/2	3476.5	3476.5	3257.6	3256.6
		-3/2	3481.2	3480.2	3271.4	3272.5
	-1/2	3/2	3529.0	3528.1	3292.7	3292.8
		1/2	3531.9	3531.8		3308.7
		-1/2	3535.4	3535.5		3324.6
		-3/2	3538.7	3539.1		3340.6
	1/2	3/2		3588.4		3361.7
		1/2		3592.6		3377.7
		-1/2	3596.5	3595.8	3393.0	3393.6
		-3/2	3600.5	3599.4	3410 (2)	3409.6
	3/2	3/2	3650.6	3650.1	3431 (2)	3431.7
		1/2	3654.3	3653.7	3446.0	3447.6
		-1/2	3659.0	3657.4	3465 (2)	3463.6
		-3/2	3663.1	3661.1		3479.5
5/2	3/2	3712.6	3713.1		3502.6	
	1/2	3716.8	3716.7	3520 (2)	3518.5	
	-1/2	3720.4	3720.4	3535 (2)	3534.5	
	-3/2	3724.1	3724.9		3550.4	
7/2	3/2	3772.2	3772.8		3571.1	
	1/2	3776.6	3776.5		3587.1	
	-1/2	3780.4	3780.2		3603.0	
	-3/2	3784.3	3783.9		3619.0	

a small amount of s character and the value of $|A_{\text{iso}}(^{47,49}\text{Ti})|$ appears to have a maximum value of about 20 G. For example, in the complex titanium acetylacetonate,¹⁴ this hyperfine parameter is about 15 G (with $g_{\parallel} = 2.000$ and $g_{\perp} = 1.921$). The predominant d character of the unpaired electron is essentially due to the symmetry restrictions of the near octahedral field.

In TiF₃, the Ti³⁺ ion is being observed for the first time in a pure D_{3h} (presumably) crystal field in which the ground state is ${}^2A_1'$. The unpaired electron now has predominantly s character, as might be expected for a hybridized orbital in a crystal field with no repulsive contributions from axial anions. $|A_{\text{iso}}(\text{Ti})|$ is now 180 G, clearly reflecting the different environment.

TiF₂. The TiF₂ ESR spectrum is much weaker than the ESR spectrum of TiF₃. Only broad lines with no evidence of hyperfine structure were observed. Assuming that the breadth of the lines is due to overlapping fluorine hfs, one can estimate the A -tensor components, i.e., obtain maximum possible values. These values are listed in columns 7, 8, and 9 of Table IV. As in TiF₃, they are quite small and again indicate that the unpaired electrons are localized on the Ti atom. If the electrons had considerable Ti 4s character then the ^{47,49}Ti hfs could also be observed, but unfortunately the lines are too weak to permit such low abundance signals to be seen. Hence, unlike TiF₃, a more exact description of the wave function of the unpaired electrons in TiF₂ cannot be obtained from these ESR spectra.

Table IV. Magnetic Parameters for Triplet TiF₂ in Solid Neon and Argon Matrices at 4 K^a

Matrix	g_x	g_y	g_z	$ D $ (cm ⁻¹)	$ E $ (cm ⁻¹)	$ A_x^F $ (MHz) ^b	$ A_y^F $ (MHz) ^b	$ A_z^F $ (MHz) ^b
Neon	1.9149 (3)	1.9229 (3)	1.9880 (3)	0.0782 (2)	0.0021(1)	27 (20)	27 (20)	56 (40)
Argon	1.9199 (3)	1.9207 (3)	1.9899 (3)	0.0785 (2)	0.0019 (1)	27 (20)	27 (20)	56 (40)

^a The z axis is parallel to the F-F direction in the bent molecule. ^b Estimated (see text).

Table V. Comparison of the Calculated and the Observed ESR Lines for TiF₂ in Solid Neon and Argon at 4 K (ν 9.386 GHz for Neon and ν 9.385 GHz for Argon)

Line	Neon		Argon	
	Obsd (G) ^a	Calcd (G)	Obsd (G) ^a	Calcd (G)
$\Delta m = 2$	1646	1648	1647	1646
z_1	2506	2504	2501	2499
y_1	2968	2970	2978	2978
x_1	3050	3051	3040	3038
x_2	3893	3890	3884	3886
y_2	3950	3949	3950	3950
z_2	4239	4242	4238	4240

^a Accuracy ± 3 G.

Both the IR evidence¹ and the ESR spectrum indicate that TiF₂ is a bent molecule. Walsh's treatment for AB₂ molecules¹⁵ has been extended by Weltner and McLeod¹⁶ and by Hayes¹⁷ to include d orbitals on the central atom. Placing 18 electrons into either scheme produces either a ¹A₁(\bar{a}_1')², a ¹A₁(b_1'')², or a ³B₁(\bar{a}_1')(b_1'') ground state.¹⁸ Excluding the possible small contributions from Ti 4p orbitals, the b_1'' orbital is a nonbonding d_{xy} orbital on Ti. (Here the y direction is the C₂ axis of symmetry and x is perpendicular to the plane of the molecule. Note that here the z axis in TiF₂ is always chosen in the F-F direction which is the usual choice for near-linear molecules in ESR but contrary to the other natural choice, i.e., along the C₂ axis) The \bar{a}_1' orbital can correspondingly be written crudely as $[s + d_{x^2-y^2} - (p_F + p_{\bar{F}})]$ which is bonding between p orbitals on fluorine but antibonding to Ti. If the bonding between the fluorine atoms is weak, as might be expected if the molecule is ionic, then these are essentially d_{xy} and $s + d_{x^2-y^2}$ nonbonding titanium orbitals perpendicular to the plane of the molecule. If almost degenerate then the triplet state, ³B₁, would lie lowest, accounting for the observed ESR spectrum.

Since the \bar{a}_1' and b_1'' orbitals are largely nonbonding, the energy of each of these orbitals is presumably not very angle dependent. The bending of the molecule results from the angular dependence of the strongly bonding b_2' (π_g) [$d_{yz} + (p_F - p_{\bar{F}})$] and a_1' (π_u) [$d_{x^2-y^2} + (p_F + p_{\bar{F}})$] orbitals at lower energy.

The relative magnitudes of the Δg_i 's observed for TiF₂ can also be rationalized if the lowest excited orbitals are the \bar{a}_2'' [$d_{xz} - (p_x - p_{\bar{x}})_F$] and \bar{b}_2' [$d_{yz} - (p_F - p_{\bar{F}})$] antibonding orbitals. If we ignore the fluorine contributions, then to second order the Δg_i 's are given by

$$\Delta g_z = 0$$

$$\Delta g_x = \Delta g_y = -2\lambda \left(\frac{1}{\Delta E_{b_2}} + \frac{1}{\Delta E_{a_2}} \right)$$

In higher order and with better wave functions, Δg_z will no longer be zero and $\Delta g_x \neq \Delta g_y$.

A question left unanswered here, because ^{47,49}Ti hfs was not observed in the relatively weak, broad lines in the TiF₂ spectra, is the degree of 4s character in the \bar{a}_1' ($s + d_{x^2-y^2}$) nonbonding orbital. A relevant case for comparison with the TiF₂ radical

is the TiF₂⁺ ion as observed in methanol.¹⁹ For the ion $g_{av} = 1.9465$ and $A_{iso}(\text{Ti}) = 50$ MHz, $A_{iso}(\text{F}) = 21$ MHz. Since the hfs is small, it indicates that the one unpaired electron is on the Ti ion in a nonbonding d orbital. This then supports the assignment of at least one of the orbitals occupied by the unpaired electrons in neutral TiF₂ to a (d_{xy}) or ($d_{x^2-y^2}$) Ti orbital, but the electron removed to form TiF₂⁺ could have come from the \bar{a}_1' ($s + d_{x^2-y^2}$) orbital in TiF₂. However, on the basis of the atomic levels in the Ti²⁺ ion,²⁰ one would assume that there is little s character involved and that the two unpaired electrons in TiF₂ occupy d_{xy} and $d_{x^2-y^2}$ orbitals on Ti perpendicular to the plane of the bent molecule.

The observed $|D| = 0.078$ cm⁻¹ in TiF₂ is also of interest. If it is assumed that it arises from interactions between electron spins essentially in d_{xy} and $d_{x^2-y^2}$ orbitals on a Ti²⁺ ion, then its magnitude is noteworthy. Since spin-orbit coupling effects also contribute to the zero field splitting,²¹ it is rather surprising to find such a small D value for electron interactions on a relatively heavy atom. A comparison can be made with VO,²² where the ground state is ⁴ Σ not ³ Σ , but the three unpaired electrons are in a similar $4s\sigma$ $3d\delta^2$ configuration. There it is only known that $D \gg h\nu \approx 0.3$ cm⁻¹, which is the expected high value.

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