Spectroscopy of MnF: Rotational Analysis of the $d^{5}\Pi - a^{5}\Sigma^{+}(0,0)$ Band

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The (0,0) band of the $d^5\Pi - a^5\Sigma^+$ system of MnF has been studied by laser-induced fluorescence in a supersonic-jet molecular beam apparatus employing a laser vaporization source. A spectrum with a rotational temperature of about 50 K has been recorded at a resolution of 0.1 cm⁻¹ and the rotational lines assigned. Most of the 18 assigned branches are shown to be satellite branches. The spectrum has been reduced using the appropriate Hamiltonian matrices and the previously derived molecular constants for the $a^5\Sigma^+$ state. A set of molecular parameters has been derived for the $d^5\Pi$ state and are interpreted in terms of $\cdots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 5\pi^1$ leading electron configuration in which the 5π molecular orbital is essentially an Mn(5p) orbital. © 1992 Academic Press, Inc.

INTRODUCTION

High-resolution spectroscopy of transition-metal-containing molecules is a field that has grown at a tremendous rate over the past 10 years. This is attributed to both improved experimental techniques, whereby fine and hyperfine structures can be resolved, and the availability of ab initio calculations which provides reliable zero-order pictures about the electronic structures.

Among the possible diatomics in which one 3d transition metal atom is bound to a group 14-17 atom of the 2nd or 3rd period, the most challenging ones are those involving Cr, Mn, and Fe because they give rise to many low-lying states of high spin multiplicity which often are heavily perturbed. For a given ligand atom the spin multiplicity peaks at Mn because the Mn ground electron configuration is $... 4s^2 3d^5$ in which the five d electrons are high spin coupled. As a result, theoretical and experimental data on Mn-containing molecules are sparse, and for those systems for which data exist they are in most instances incomplete. There are only four species for which reliable data exist. These are MnO, MnS, MnH, and MnF. The spectroscopy of MnO has recently been reviewed by Merer (1), who also discusses all of the other possible 3d transition metal monoxides. Reliable work on MnS is limited to the $A^{6}\Sigma^{+}$ - $X^{6}\Sigma^{+}$ system, which has been studied both at Doppler and sub-Doppler resolution by Douay et al. (2, 3). The MnH species has recently been the subject of extensive investigations by Balfour (4), Balfour et al. (5), and Varberg et al. (6, 7). The beautiful work of Varberg et al. (7) on the $A^{7}\Pi - X^{7}\Sigma^{+}(0,0)$ band at the sub-Doppler resolution of about 100 MHz provided invaluable insights into the bonding of this molecule.

Work on MnF arises as a logical extension of the work on MnH. These two species have similar electronic structures because both ligand atoms are short of one electron from closed shell.

Recently, we reported the first rotational, fine and hyperfine analysis of any band system in MnF (8). In particular, this work dealt with the (0,0) and (1,1) bands of the $c^5\Sigma^+ - a^5\Sigma^+$ system. Internal hyperfine perturbations in the $c^5\Sigma^+$ state were observed and discussed, and the nature of the electronic states was rationalized from the hyperfine parameters. In a continuing effort to rationalize the bonding in this challenging species, we recently investigated the (0,0) band of the $d^5\Pi - a^5\Sigma^+$ system, which lies near 504 nm. This system is presumably the analogue to the 480-nm system of MnH (9).

The 504-nm system of MnF was first studied by Bacher (10) and then by Hayes (11). Unfortunately, due to the intrinsic complexity of the spectrum, compounded with the high temperature of the source, no reliable interpretation was obtained. A more recent study by Launila (12) using a hollow cathode source both with Fourier transform and grating spectrograph techniques also failed to produce an assignable spectrum. It was then clear that a much lower temperature spectrum was required. We recently recorded the same spectrum at a rotational temperature of about 50 K using a laser vaporization source in a molecular beam apparatus. Although the resolution was limited to about 0.1 cm^{-1} (laser limited), since the $a^5\Sigma^+$ state constants were known from our previous study the spectrum could assigned and reliable constants derived. This analysis is reported herein.

EXPERIMENTAL PROCEDURE

The experimental procedure has been described in detail in our previous publication (8). Only a brief description is given here. The MnF molecules were produced in a free-jet molecular beam apparatus by laser vaporization of Mn metal (99.99%) in the presence of a Helium carrier gas doped with <0.5% of SF₆. Fluorescence from the molecules was excited with a XeCl excimer pumped Lumonics Hyperdye 300 pulsed dye laser operating in the C500 dye region. The dye laser frequency was scanned with increment of 0.02 cm⁻¹ and then 10 shots were averaged for each frequency. The total recording time for the spectrum was about 6 h. The experimental resolution was made with a Candela LS-1 laser spectrometer with an accuracy of 0.4 cm⁻¹ in the 500-nm region.

APPEARANCE OF THE SPECTRUM

The spectrum shown in Fig. 1 consists of five rather equally spaced subbands. A number of very distinct satellite branches can be seen mainly on the high wavenumber side of the subbands. The rotational temperature of the spectrum is about 50 K. Sudden intensity drops can be seen in three of the branches, the last lines with normal intensity being ${}^{O}Q_{24}(19)$, ${}^{O}R_{12}(15)$, and ${}^{U}R_{52}(15)$ in the respective branches. A sequence of partly unassigned head-like features can be seen on the low frequency side of the fifth subband. The wavenumbers of the assigned lines are given in Table I.

ENERGY LEVEL EXPRESSION

The Hamiltonians are written in a case (a) basis set using the same definitions of parameters as in Ref. (5); N = J - S,



FIG. 1. Fluorescence excitation spectrum of the (0,0) band of the $d^{5}\Pi - a^{5}\Sigma^{+}$ system of MnF at a resolution of 0.1 cm⁻¹.

$$H = T + BN^{2} - DN^{4} + \gamma N \cdot S + [\lambda + \lambda_{D}N^{2}, S_{z}^{2} - \frac{1}{3}S^{2}]_{+} + \frac{1}{2}[A + A_{D}N^{2}, L_{z}S_{z}]_{+} + \frac{1}{4}[(o + p + q), S_{+}^{2} + S_{-}^{2}]_{+} - \frac{1}{4}[(p + 2q), J_{+}S_{+} + J_{-}S_{-}]_{+} + \frac{1}{4}[q, J_{+}^{2} + J_{-}^{2}]_{+},$$
(1)

where $[x, y]_+$ denotes the anticommutator xy + yx.

The higher-order parameters η and θ according to Brown and Milton (13), and Cheung *et al.* (14) are also needed:

$$\left\langle S\Sigma | H_{\rm SO}^{(3)} | S\Sigma \right\rangle = \eta \Lambda \Sigma \left\{ \Sigma^2 - \frac{1}{5} [3S(S+1) - 1] \right\}$$
(2)

$$\langle S\Sigma | H_{SO}^{(4)} | S\Sigma \rangle$$

= $\frac{1}{12} \theta \{ 35\Sigma^4 - 30S(S+1)\Sigma^2 + 25\Sigma^2 - 6S(S+1) + 3S^2(S+1)^2 \}.$ (3)

The explicit forms of all the matrix elements can be found in Ref. (8), where also some additional terms not needed in this work are listed.

RESULTS AND ANALYSIS

The analysis was carried out in two steps. Initial trial values for the $d^5\Pi$ parameters were first guessed and a spectrum was synthesized using these parameters together with the well-known parameters for the $a^5\Sigma^+$ state. Calculated Hönl-London factors were used together with the known rotational temperature of 50 K to include intensity information. Several of the most prominent branches could be identified in this way. Also, the intensity distribution seemed to favor the hypothesis that the $d^5\Pi$ state was inverted.

In the second part of the analysis, the numberings were altered in a systematic way and fits were made at every step to the $a^5\Sigma^+$ Hamiltonian with all the constants

J	R ₁	R ₃	P ₃	P ₄	\$R ₂₁	RQ21	1
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 3 22 4 25	19659.52 19661.54 19663.79 19665.71 19667.64 19667.69 19673.60 19673.60 19675.43 19677.39 19679.21	19811.72 19812.41 19813.01 19813.54 19814.12 19814.68 19815.15 19815.64 19816.83 19817.30	19806.55 19805.66 19804.73 19803.80 19803.11 19801.97 19801.00 19798.90 19798.90 19797.80 19796.83 19795.65 19794.60	19885.75 19884.15 19882.53 19880.88 19879.24 19877.63 19877.63 19877.63 19877.63 19877.63	19736.90 19739.06 19741.12 19743.45 19745.65 19747.59 19751.82 19753.75 19755.78 19755.78 19755.78 19755.78 19763.47 19756.35 19763.47 19765.71 19770.73 19770.73 19772.54 19774.37 19776.12 19777.78	19732.55 19733.99 19735.62 19736.90 19738.40 19739.76 19741.13 19742.49 19743.73 19745.04 19746.35 19747.59 19748.80 19749.89 19751.15 19752.28 19753.35 19754.62 19755.78 19755.77 19757.77	2 3 4 5 6 6 7 8 9 9 10 11 12 13 14 15 16 17 18 19 20 21 22 3 24 25
J	QR ₁₂	PQ45	^T R ₃₁	sQ ₃₁	NP ₁₃	0Q ₂₄]
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 22 22 22 22 22 22 22 22	19649.75 19651.04 19652.32 19653.64 19655.12 19656.36 19657.71 19658.95 19660.20 19661.54 19662.72 19663.79 19664.92 19666.14 19667.12 19668.23 19669.33 19670.56 19671.69 19672.60 19673.60	19880.45 19878.83 19877.13 19875.42 19873.62 19873.62 19870.13 19868.47 19866.71 19866.71 19865.00 19863.13 19861.40	19819.69 19821.98 19823.94 19825.93 19828.03 19829.95 19833.82 19835.67 19837.62 19837.62 19837.62 19839.39 19841.25 19843.05 19844.81 19846.53 19844.82 19849.92 19851.70 19853.32 19855.05	19814.68 19816.21 19817.76 19819.20 19820.65 19821.98 19823.48 19824.89 19826.27 19827.68 19829.02 19830.38 19831.85 19833.10 19834.35	19639.91 19639.13 19638.20 19637.29 19635.47 19634.59 19633.65 19632.69 19631.67 19630.70 19629.69 19628.49 19627.48	19726.41 19725.66 19724.78 19723.90 19723.00 19722.10 19721.22 197720.29 19719.22 19718.30 19717.39 19716.30 19715.14 19714.10 19712.96 19711.77 19710.67	3 4 4 5 6 7 7 8 9 9 10 11 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
J	0Q35	UR41	TQ ₄₁	UR52	TQ52	NQ14	J
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 22 22	19804.73 19803.11 19801.61 19800.02 19798.42 19796.83 19795.30 19793.67 19792.02 19790.40 19788.86	19894.50 19896.79 19898.72 19900.74 19902.95 19907.00 19909.06 19911.10 19913.16	19892.42 19893.98 19895.46 19896.77 19898.13 19899.44 19900.75 19902.02 19903.32 19904.61 19905.80 19907.02 19908.23 19907.02 19908.23 19910.54 19911.60 19912.88 19913.73 19915.03	19961.65 19963.15 19964.67 19966.08 19967.45 19970.21 19971.45 19972.72 19973.96 19975.25 19976.58 19977.67 19978.73 19979.94 19980.93 19982.00 19983.09 19984.18 19985.23	19959.45 19960.20 19960.91 19961.65 19962.36 19963.15 19963.70 19964.25 19964.67 19965.75	19639.56 19638.70 19637.85 19635.88 19635.97 19635.04 19634.10 19633.05 19632.14 19631.12 19630.18 19629.03 19627.94 19626.84	2 3 4 5 6 7 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 21 22

Observed Line Positions (cm⁻¹) for the (0,0) Band of the $d^5\Pi$ - $a^5\Sigma^+$ System of MnF

fixed to the previously reported values (8). At every iteration, a term value scheme for the $d^5\Pi$ state was generated and fitted independently and a new spectrum was synthesized. In total 18 branches were assigned in this way. The fits to the $d^5\Pi$ state were made for both inverted and regular cases. No significant differences were found in the RMS values for these two cases, but some lines interpreted as first lines in the branches, particularly the presumed ${}^{T}Q_{52}(2)$ line at 19 959.45 cm⁻¹, again indicated that the $d^5\Pi$ state was inverted. The fits were also made both using spin-orbit parameters including the higher-order ones, and letting the band origin float freely. Again, no significant differences were noted in the RMS errors of the fits. It was rather surprising that all the spin-orbit parameters, including η and θ , seemed to be well determined. The derived molecular constants for the $d^5\Pi$ state are given in Table II. The synthetic spectra also reproduce almost all the unresolved heads of the observed spectrum. The locations, intensities, and assignments of the heads of the (0,0) band are presented in Table III.

A sequence of heads between the fourth and fifth subbands is *not* reproduced by the synthetic spectra of the (0,0) band. These heads are interpreted as a vibrational sequence consisting of F_5 heads in the (v, v) bands, where $0 \le v \le 6$. These heads are given in Table IV. It seems surprising that these heads should be members of a vibrational sequence because it was observed in our previous work (8) that the intensity relation between the (0,0) and (1,1) bands of the $c^5\Sigma^+ - a^5\Sigma^+$ system was

	a ⁵ Σ+	d⁵∏
т	0.609 ^b	19806.76(40) ^c
A A _D		-78.2661(75) -0.003644(33)
В	0.373262(16)	0.363007(50)
10 ⁷ D	5.134(16)	0 (fixed)
γ	-0.002053(78)	0 (fixed)
λ	0.41390(53)	-0.8886(32)
10 ⁵ λ _D	-3.221(76)	-16.3(1.5)
η		0.3501(47)
θ		-0.1640(20)
o+p+q		-0.0562(85)
p+2q		0.0310(56)
q		-0.00762(35)
r ₀ (Å)	1.788650(38)	1.81374(13)
RMS of fit		0.088

TABLE II

 a) The numbers in parentheses are the uncertainties (1σ) in the units of the last quoted decimal place.

b) The $a^5\Sigma^+$ constants have been taken from Ref.(3) with the exception that the T value is now chosen so that the J = 2 level of the F₁ component of $a^5\Sigma^+$ has been set to zero.

c) The uncertainty in the T value is due to the absolute calibration uncertainty of the Candela LS-1 instrument.

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Wavenumber ^a	Assignment	Intensity
19642.7	0 _{Q13}	3
19728.9	PR24	3
19809.5	Q3	4
19888.6	R ₄ , ^R P ₄₂	6
19958.0	SQ53, SP52	8

	TAB	LE III
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Relative Intensities of the Heads of the (0,0) Band of the $d^{5}\Pi a^{5}\Sigma^{+}$ System of MnF

^a The wavenumbers refer to the centers of the heads.

approximately an order of magnitude, which means a vibrational temperature significantly less than 1000 K. If, on the contrary, the vibrational temperature was calculated using the intensities of the heads of the F_5 vibrational sequence, then we would arrive at a vibrational temperature of 3000-4000 K (neglecting the Franck-Condon factors). An immediate conclusion is that the studied sample is far from thermodynamic equilibrium, especially considering that no such sequences are seen near the other subbands. However, the heads with $v \le 4$ can be fitted with an average accuracy of 0.1 cm⁻¹ to the well-known expression

$$T'_{e} + \omega'_{e}(v + \frac{1}{2}) - \omega_{e} x'_{e}(v + \frac{1}{2})^{2} - \omega''_{e}(v + \frac{1}{2}) + \omega_{e} x''_{e}(v + \frac{1}{2})^{2}, \qquad (4)$$

where $\omega_e'' = 645.92 \text{ cm}^{-1}$ and $\omega_e x_e'' = 3.22 \text{ cm}^{-1}(8)$. The corresponding vibrational constants of the upper state obtained from the fit are $\omega_e' = 640.0 \text{ cm}^{-1}$ and $\omega_e x_e' = 3.6 \text{ cm}^{-1}$. Our conclusion is that this sequence must be a vibrational sequence of F_5 heads despite the fact no such sequences are seen near the other subbands. We have at present no explanation to this asymmetry. A comparison with a recording of the $b^5\Pi - a^5\Sigma^+$ system near 832 nm has been made. This system also shows vibrational sequences of the same type. However, these sequences are more numerous in the 832-nm system, since these are found also in the F_1 , F_2 , and F_5 subbands. Further studies will be initiated to clarify this matter.

The intensities of the observed branches are as follows:

The intensities of the unresolved branches are put in parentheses. The intensities can be compared to those in CrO (14). Some similarities can be noted, especially the relatively high intensities of the satellite branches compared to the main branches.

Т	`A	BI	Æ	Г	٧
			_		٠

Band	Wavenumber ^a	Intensity
(6,6)	19909.2	1
(5,5)	19918.1	1
(4,4)	19927.0	3
(3,3)	19935.8	5
(2,2)	19943.8	6
(1,1)	19951.4	7
(0,0)	19958.0	8

Relative Intensities of the F_5 Heads of the (v', v'') Bands $(v'' = v', 0 \le v \le 6)$ of the $d^5\Pi - a^5\Sigma^+$ System of MnF

^a The wavenumbers refer to the centers of the heads.

The molecular constants given in Table II are compatible with the observed hightemperature hollow cathode spectra. This has been verified by synthesizing the hightemperature spectra with these constants and by comparing these spectra with the observed ones. However, due to many overlaps and particularly due to the hyperfine broadened line profiles in the hollow cathode spectra, it has not been possible to obtain an immediate "branch-to-branch" correspondence between the spectra in the same way as in Ref. (8).

DISCUSSION

In our previous work (8), it was shown that the $a^5\Sigma^+$ state contains an important fraction of the $\cdot \cdot \cdot 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 10\sigma^1$ electron configuration, although it was made unequivocal that this configuration alone was insufficient to describe completely the a state. In a first approximation, the 8σ and 3π molecular orbitals (MOs) are $F(2p_{\sigma})$ and $F(2p_{\pi})$, respectively. The 9σ , 1δ , and 4π MOs are essentially Mn(3d) in character, in which the electrons are coupled in a high spin $d^5({}^6S)$ configuration. The 10σ MO is a nonbonding MO formed by hybridization of the Mn(4s) with Mn(4p) orbital. This MO points away from the ligand so it does not shield the Mn⁺² ion core from the electrostatic attraction of the F⁻ ligand.

The $d^5\Pi$ state is the second excited ${}^5\Pi$ state of MnF. The first one is the *b* state which lies about 12 000 cm⁻¹ above the $a^5\Sigma^+$ state. By analogy with MnH (15), the electron configuration giving rise to the $b^5\Pi$ state is likely $\cdots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^3$ in which the Mn⁺ ion core is $3d^6$ (6D). The electron configuration of the $d^5\Pi$ state for both MnH and MnF has not been predicted theoretically (neither are the other states of MnF). However, the experimental data and physical intuitions indicate that it is likely to be $\ldots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 5\pi^1$ where the 5π MO has a large Mn(4p) character and the 9σ , 1δ , and 4π electrons are coupled in a high spin $d^5({}^6S)$ configuration. The $d^5\Pi$ state would then arise from the coupling of the 4p electron with the $d^5({}^6S)$ configuration. The $a \rightarrow d$ transition therefore corresponds to a promotion of the nonbonding 10σ electron to the 5π MO. Supports for this interpretation is provided by (1) the increase in bond length upon excitation, and (2) the sign and magnitude of the first order spin orbit constant, A. We now discuss these two points in more details. (1) The increase in bond length. The increase in bond length upon excitation indicates that an electron is promoted from a particular orbital to either a more antibonding or a more shielding orbital. Here, the increase of 0.025 Å can be attributed solely to a more shielding orbital. The Mn(4p) orbital is indeed more shielding than the 4s-4p hybrid giving rise to the highly back-side polarized 10σ MO, and consequently the bond length must increase upon excitation.

(2) The first-order spin-orbit constant. This is our strongest support for the proposed electron configuration. Since the $d^{5}\Pi$ state is derived from the coupling of the 4p electron with the $d^{5}({}^{6}S)$ core of Mn⁺⁺, the determinantal wavefunction for the ${}^{5}\Pi_{3}$ component ($\Sigma = S$) is (16)

$$|d^{5}\Pi_{3}\rangle = \frac{1}{\sqrt{30}}(5\Phi_{1} - \Phi_{2} - \Phi_{3} - \Phi_{4} - \Phi_{5} - \Phi_{6}), \qquad (5)$$

where the Φ 's are the primitive spin orbitals defined as

 $\Phi_{1} = |\sigma\alpha\delta^{+}\alpha\delta^{-}\alpha\pi_{4}^{+}\alpha\pi_{4}^{-}\alpha\pi_{5}^{+}\beta|$ $\Phi_{2} = |\sigma\alpha\delta^{+}\alpha\delta^{-}\alpha\pi_{4}^{+}\alpha\pi_{4}^{-}\beta\pi_{5}^{+}\alpha|$ $\Phi_{3} = |\sigma\alpha\delta^{+}\alpha\delta^{-}\alpha\pi_{4}^{+}\beta\pi_{4}^{-}\alpha\pi_{5}^{+}\alpha|$ $\Phi_{4} = |\sigma\alpha\delta^{+}\alpha\delta^{-}\beta\pi_{4}^{+}\alpha\pi_{4}^{-}\alpha\pi_{5}^{+}\alpha|$ $\Phi_{5} = |\sigma\alpha\delta^{+}\beta\delta^{-}\alpha\pi_{4}^{+}\alpha\pi_{4}^{-}\alpha\pi_{5}^{+}\alpha|$ $\Phi_{6} = |\sigma\beta\delta^{+}\alpha\delta^{-}\alpha\pi_{4}^{+}\alpha\pi_{4}^{-}\alpha\pi_{5}^{+}\alpha|$

The diagonal matrix elements for the spin orbit operator, H_{so} , are given by (17)

$$\langle \Lambda, \Sigma, S, \Omega | H_{\rm SO} | \Lambda, \Sigma, S, \Omega \rangle = A\Lambda\Sigma,$$
 (6)

where A is the first-order spin-orbit coupling constant. For the $d^5\Pi_3$ component this matrix element is

$$\left\langle d^{5}\Pi_{3} | H_{\rm SO} | d^{5}\Pi_{3} \right\rangle = 2A. \tag{7}$$

The spin-orbit operator may be written as (17)

$$H_{\rm SO} = \sum_{i} \hat{a}_{i} \mathbf{l}_{i} \cdot \mathbf{s}_{i}, \qquad (8)$$

which after expansion becomes (17)

$$H_{\rm SO} = \sum_{i} \left[\hat{a}_i \mathbf{l}_{iz} \cdot \mathbf{s}_{iz} + \frac{1}{2} \hat{a}_i (\mathbf{l}_i^+ \mathbf{s}_i^- + \mathbf{l}_i^- \mathbf{s}_i^+) \right]. \tag{9}$$

The summation extends over all of the open shell electrons. Inserting Eq. (9) in Eq. (7) and using the wavefunction in Eq. (5), one obtains

$$A = -\frac{1}{6}\,\hat{a}_{5\pi},\tag{10}$$

where $\hat{a}_{5\pi} = \langle 5\pi | \hat{a} | 5\pi \rangle$. Equation (10) clearly indicates that the state should be inverted, as observed. Now, making the approximation that the 5π MO is a pure Mn(4*p*) orbital, Eq. (10) reduces to

$$A = -\frac{1}{6}\zeta_{4p}.\tag{11}$$

The value of ζ_{4p} is not readily available but can be estimated from atomic data (18, 19) to be about 380 cm⁻¹ for Mn⁺. This yields $A(d^5\Pi)_{calc.} = -63$ cm⁻¹ in good agreement with the experimental value of -78 cm⁻¹, thus supporting the proposed $\cdot \cdot 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 5\pi^1$ electron configuration. One possible cause for the small discrepancy is the contamination of the 9σ MO which is essentially a pure Mn $3d\sigma$ orbital. This can arise either by hybridization with the Mn $4p\sigma$ orbital to produce an orbital pointing away from the F⁻ ligand, or by a bonding interaction with the F⁻ $2p\sigma$ orbital.

The A-value for the corresponding ⁵II state of MnH has recently been determined to be -23 cm^{-1} by Balfour *et al.* (9), in poor agreement with the calculated value of -63 cm^{-1} . This should not be interpreted as an indication that the single $\cdots 7\sigma^2$ $[6\sigma^2 3\pi^2 1\delta^2]_{Mn3d} [4\pi^1]_{Mn4p}$ configuration is insufficient to describe the d^5II state but simply reflects the more covalent nature of the bonding in MnH. In MnH, the 7σ MO results from the bonding interaction between the Mn 4σ and H 1s orbitals whereas in MnF the 8σ MO is essentially a pure F $2p\sigma$ orbital. Since 4s electrons shield 4pelectrons from the nuclear charge, the A-value should be less in MnH than in MnF, and less than calculated for the ionic Mn⁺H⁻ model, in agreement with observations.

CONCLUSION

We reported here the first rotational analysis of the $d^5\Pi - a^5\Sigma^+(0,0)$ band of MnF and derived molecular parameters for the $d^5\Pi$ state. It has been proposed that this state arises from the $\cdots 8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 5\pi^1$ electron configuration in which the 5π MO is essentially an Mn(4p) orbital, and this is supported by the sign and magnitude of the first order spin orbit coupling constant. Work at sub-Doppler resolution will be initiated in the near future in order to obtain more physical insights on this state. Finally, we hope that this work will stimulate theorists to undertake ab initio calculations on this challenging molecule.

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