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Molecules in high spin states II: the pure rotational spectrum of MnF ($X^7\Sigma^+$)

P.M. Sheridan¹, L.M. Ziurys^{*}

Department of Chemistry, Department of Astronomy, Steward Observatory, University of Arizona, 933 North Cherry Avenue, Tucson, AZ 85721, USA

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Abstract

The pure rotational spectrum of MnF has been measured in its $X^7\Sigma^+$ ground state using millimeter/sub-millimeter direct absorption methods. Five and six rotational transitions, respectively, were recorded for this radical in its v = 0and v = 1 states in the range 338–630 GHz. MnF was created from SF₆ and manganese vapor, produced in a Broidatype oven. The species exhibited a complex pattern where the fine and ⁵⁵Mn and ¹⁹F hyperfine structures are intermixed. Rotational, spin-rotation, spin-spin and hyperfine parameters have been determined for MnF. These constants have been interpreted in terms of bonding and electronic structure in metal fluorides.

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1. Introduction

The spectra of even small 3d transition metal compounds are usually quite complex. The complexity arises from the presence of 3d electrons, which give rise to a multitude of closely spaced electronic states [1]. Determination of the ground electronic term of these molecules is consequently quite problematic. For example, the ground state of TiF over the years has been assigned as ${}^{4}\Sigma$ [2], ${}^{2}\Delta$ [3], and ${}^{4}\Phi$ [4,5]. The ground state of FeN has still yet to be conclusively determined, although it is most likely to be $^{2}\Delta$ or ⁴Π [6].

Perhaps some of the most complicated spectra of molecules containing 3d transition metals are those with manganese. The element has a $4s^23d^5$ electron configuration and hence a half-filled 3d shell. Therefore, extremely high multiplicities and orbital angular momentum values can be generated in manganese compounds, as evidenced by even the simplest of these species, MnH [7-9]. Measurements of the $A^7\Pi \rightarrow X^7\Sigma^+$ transition of this radical have necessitated a detailed analysis, which has been additionally complicated by the presence of the two nuclear spins of ⁵⁵Mn (I = 5/2) and ¹H (I = 1/2) [7,8]. The hyperfine

Corresponding author. Fax: +1-520-621-1532.

E-mail address: lziurys@as.arizona.edu (L.M. Ziurys).

¹ Merck Research Fellow.

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interactions in MnH have in fact been found to be so substantial that they cause mixing of the seven spin components, destroying the 'goodness' of the J quantum number [9]. Pure rotational spectra have also been recorded for MnO [10] and MnS [11], as well, in their $X^6\Sigma^+$ ground states. In both cases, higher order fine and hyperfine constants were found necessary to fully analyze these problematic data sets. In addition, various electronic bands of MnCl have been recorded [12]; again, assignment of the transitions has proved to be difficult.

Another manganese-bearing species of interest is MnF. The earliest spectroscopic observation of this radical occurred in 1939, where two band systems were recorded [13]. More recent investigations occurred in 1978, when matrix isolation studies resulted in the determination of A_{iso} and $A_{\rm dip}$ hyperfine parameters [14]. Additional gasphase work has been conducted by Launila, Simard and collaborators (e.g. [15,16]), who recorded the $A^7\Pi - X^7\Sigma^+, c^5\Sigma^+ - a^5\Sigma^+, d^5\Pi - a^5\Sigma^+$, and $b^5 - a^5 \Sigma^+$ transitions using LIF. For these works, MnF was created in a supersonic jet using laser ablation techniques. These studies verified the ground state of MnF to be $X^7\Sigma^+$, and established a rotational constant of 0.35173 cm⁻¹. (A more complete set of spectroscopic parameters was determined for the $A^7\Pi$ state.) Ab initio calculations have not been carried out for MnF to date.

As part of our interest in investigating molecules in high spin states, as well as studying trends in 3d transition metal fluorides, we have recorded the pure rotational spectrum of MnF ($X^7\Sigma^+$) in its v = 0 and v = 1 states. Because of the presence of two nuclear spins in this radical, as well as six unpaired electrons, the observed spectra were expected to be complicated; this situation was exacerbated by the relatively small magnitude of the spin interactions, which meant that the hyperfine components associated with each spin state could not be easily distinguished. However, the spectral pattern could be sufficiently resolved such that rotational, fine structure, and hyperfine constants were obtained. Here we present these data and their analysis, and discuss the derived parameters in terms of bonding in manganese compounds and in 3d transition metal fluorides.

2. Experimental

The pure rotational spectrum of MnF was measured using one of the direct absorption millimeter/sub-millimeter-wave spectrometers of the Ziurys lab [17]. Briefly, the instrument consists of three basic parts: a radiation source composed of Gunn oscillators and Schottky diode multipliers, a high temperature reaction chamber containing a Broida-type oven, and an InSb bolometer detector. Offset ellipsoidal mirrors are used as the focusing elements and a pathlength modulator is employed for baseline smoothing. The radiation is FM modulated at ± 25 kHz and detected at 2f by a lock-in-amplifier.

The MnF radical was synthesized by the reaction of Mn vapor, produced in a Broida-type oven, with approximately 20 mTorr of SF_6 gas. The reactant gas was added to the reaction cell from underneath the oven. Production of the MnF radical was not found to increase upon addition of a carrier gas such as Ar or by employing a d.c. discharge; hence, neither was used. During the reaction, no chemiluminescence was observed.

Final frequency measurements of each rotational transition were obtained by averaging an even number of scan pairs 5 MHz wide, one taken in increasing and the other in decreasing frequency. Gaussian line shapes were then fit to these averages. For the lower frequency transitions and those in the v = 1 state, up to 6 such pairs were found to be necessary to achieve an adequate signal-to-noise ratio. Typical line widths ranged from 850 kHz at 338 GHz to 1700 kHz at 628 GHz. Many features appeared to be broader, a result of line blending.

3. Results

Manganese has a spin of $I_1 = 5/2$, and ¹⁹F has a spin of $I_2 = 1/2$. Consequently, to a first approximation, every rotational transition in MnF(X⁷ Σ^+) is split into $(2S + 1)(2I_1 + 1)$ $(2I_2 + 1) = 84$ separate fine structure/hyperfine components. However, the spin interactions are sufficiently small in manganese fluoride such that the hyperfine transitions originating in each separate spin component overlap. Hence, one continuous spectrum of numerous congested and partially blended transitions results. Such a pattern is not found in either MnO($X^6\Sigma^+$) or MnS($X^6\Sigma^+$). In these cases, the spin components are sufficiently spaced in frequency that their respective hyperfine patterns are clearly separated. Furthermore, both these molecules only have a single nuclear spin.

Typical spectra showing the convoluted pattern in MnF in its v = 0 state are presented in Fig. 1. Here the $N = 17 \leftarrow 16$, $19 \leftarrow 18$, and $23 \leftarrow 22$ rotational transitions are displayed. A clear fine structure and/or hyperfine pattern are not apparent in these data. The 84 individual transitions are compressed into a 100 MHz range, and hence there are many blended lines, further confused because of the second derivative line shapes. Several individual features are present in these data, however, especially at the extrema of each rotational hypermultiplet. (The largest hyperfine splittings are expected for the F_1 : J = N + 3 and F_7 :J = N - 3 spin components [9], which are at the lowest and highest frequency end of a given transition.) Other individual transitions are also discernable midway through the morass of lines. Several repeating features are traced by dashed lines in the figure in successive spectra. The v = 1 data are very similar in appearance.

Transition frequencies established from these spectra are presented in Table 1. As the table illustrates, five transitions were measured for MnF in the v = 0 state. Listed here are the frequencies of all spectra lines that could be resolved in the complex pattern, a total of 319 features considering all transitions. Some lines have been identified as a blend of multiple components arising from the nuclear spins; hence, the frequency appears more than once in the table. In addition, six transitions were measured for MnF in the v = 1 vibrational state. The $N = 18 \leftarrow 17$, $19 \leftarrow 18$, $22 \leftarrow 21$, $23 \leftarrow 22$, $24 \leftarrow 23$, and $30 \leftarrow 29$ transitions were





Fig. 1. Spectra of the $N = 17 \leftarrow 16$, $19 \leftarrow 18$, and $23 \leftarrow 22$ rotational transitions of MnF ($X^7\Sigma^+$) in its ground vibrational state near 359, 401, and 486 GHz, respectively. To a first approximation, each transition consists of 84 hyperfine components, arising from the electron spin and ⁵⁵Mn and ¹⁹F nuclear spins, condensed into a frequency range of about 100 MHz. These components are highly blended such that the fine/hyperfine pattern is not easily discernable in these data, although there are many repeating spectral features, which are traced by dashed lines across the spectra. Each spectrum is an average of four, one minute integrations over a 140 MHz frequency range.

Table 1 Measured Rotational Transitions for MnF $(X^7\Sigma^+)^a$

N^{\prime}	$J^{'}$	F_{1}^{\prime}	$F^{'}$	\leftarrow	Ν	J	F_1	F	v _{obs}	$v_{\rm obs-calc}$
16	14	11.5	11		15	13	10.5	10	338373.656	0.573
16	14	11.5	12		15	13	10.5	11	338373.656	0.097
16	14	13.5	13		15	13	12.5	12	338373.656	-0.296
16	13	12.5	13		15	12	11.5	12	338375.506	0.320
16	15	12.5	12		15	14	11.5	11	338377.526	-0.141
16	15	12.5	13		15	14	11.5	12	338380.387	< 0.000
16	14	12.5	13		15	13	11.5	12	338382.480	-0.091
16	13	13.5	13		15	12	12.5	12	338384.241	-0.089
16	14	13.5	14		15	13	12.5	13	338384.241	-0.152
16	16	13.5	13		15	15	12.5	12	338390.362	-0.085
16	15	13.5	14		15	14	12.5	13	338390.362	-0.195
16	16	13.5	14		15	15	12.5	13	338390.362	-0.198
16	15	13.5	13		15	14	12.5	12	338392.139	-0.305
16	16	14.5	14		15	15	13.5	13	338393.543	-0.423
16	15	15.5	16		15	15	14.5	15	338398.012	0.539
16	13	14.5	15		15	12	13.5	14	338398.012	-0.240
16	15	14.5	14		15	14	13.5	13	338398.012	-0.520
16	13	14.5	14		15	16	13.5	13	338399.826	0.257
16	13	15.5	16		15	12	14.5	15	338399.826	-0.246
16	17	14.5	15		15	16	13.5	14	338401.797	0.091
16	16	14.5	15		15	15	13.5	14	338401.797	0.012
16	15	16.5	17		15	15	15.5	16	338407.381	0.047
16	16	16.5	16		15	15	15.5	15	338407.381	0.011
16	17	15.5	15		15	16	14.5	14	338407.381	0.032
16	17	15.5	16		15	16	14.5	15	338416.014	0.317
16	17	16.5	16		15	14	14.5	15	338416.014	-0.348
16	14	15.5	16		15	13	14.5	15	338416.014	-0.580
16	14	16.5	17		15	13	15.5	16	338418.732	-0.247
16	16	17.5	18		15	15	16.5	17	338420.007	0.497
16	18	16.5	16		15	17	15.5	15	338420.007	-0.450
16	16	17.5	17		15	15	16.5	16	338421.488	0.360
16	15	16.5	16		15	14	15.5	15	338423,136	-0.578
16	16	16.5	17		15	16	15.5	16	338427.754	0.049
16	15	17.5	18		15	14	16.5	17	338429.914	0.257
16	14	16.5	16		15	13	15.5	15	338429.914	-0.118
16	17	16.5	17		15	14	15.5	16	338429.914	-0.298
16	17	18.5	19		15	16	17.5	18	338432.518	0.421
16	15	17.5	17		15	14	16.5	16	338432.518	0.321
16	18	16.5	17		15	17	15.5	16	338434.575	0.081
16	19	17.5	17		15	18	16.5	16	338436.982	-0.528
16	18	17.5	17		15	17	16.5	16	338438 512	-0.087
16	16	18.5	18		15	15	17.5	17	338439.803	0.274
16	16	18.5	19		15	15	17.5	18	338441 894	0.685
16	17	17.5	18		15	16	16.5	17	338441 894	-0.052
16	18	17.5	18		15	17	16.5	17	338441 894	-0.343
16	17	19.5	20		15	16	18.5	19	338445 119	0.285
16	17	19.5	19		15	16	18.5	18	338445 119	-0.298
16	18	18.5	18		15	17	17.5	17	338451 884	0.131
16	19	19.5	19		15	18	18.5	18	338454 072	0 541
16	18	18.5	19		15	17	17.5	18	338454 072	-0 223
16	19	19.5	20		15	18	18.5	19	338454 072	-0.219
16	18	19.5	20		15	17	18.5	19	338463 046	-0.053
16	18	10.5	10		15	17	18.5	18	338463 046	0.000
10	10	17.5	17		1.2	1/	10)	10		V.41.)

Table 1 (continued)

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$N^{'}$	$J^{'}$	F_1^{\prime}	F^{\prime}	\leftarrow	N	J	F_1	F	v _{obs}	$v_{\rm obs-calc}$
16	19	20.5	21		15	18	19.5	20	338468.192	0.209
16	19	20.5	20		15	18	19.5	19	338468.192	-0.265
16	19	21.5	22		15	18	20.5	21	338469.814	0.141
16	19	21.5	21		15	18	20.5	20	338469.814	-0.191
17	14	11.5	12		16	13	10.5	11	359484.332	0.083
17	14	12.5	12		16	13	11.5	11	359484.332	-0.139
17	14	13.5	13		16	13	11.5	12	359488.448	-0.276
17	14	12.5	13		16	13	12.5	12	359488.448	-0.573
17	15	12.5	12		16	14	11.5	11	359493.677	0.339
17	15	12.5	13		16	14	11.5	12	359493.677	-0.111
17	15	14.5	14		16	14	13.5	13	359495.558	-0.422
17	14	13.5	14		16	13	12.5	13	359497.326	0.739
17	15	13.5	14		16	14	12.5	13	359502.581	-0.016
17	15	13.5	13		16	14	12.5	12	359502.581	-0.816
17	15	14.5	15		16	14	13.5	14	359507.333	0.679
17	15	15.5	15		16	14	14.5	14	359507.333	0.390
17	16	14.5	15		16	15	13.5	14	359510.267	-0.025
17	14	14.5	15		16	13	13.5	14	359510.267	0.005
17	17	14.5	14		16	16	13.5	13	359510.267	-0.211
17	17	14.5	15		16	16	13.5	14	359510.267	-0.358
17	16	14.5	14		16	15	13.5	13	359512.125	0.011
17	16	15.5	16		16	15	14.5	15	359514.540	< 0.000
17	17	15.5	15		16	16	14.5	14	359514.540	-0.515
17	16	15.5	15		16	15	14.5	14	359517.761	-0.080
17	14	15.5	16		16	13	14.5	15	359517.761	-0.318
17	16	16.5	16		16	15	15.5	15	359517.761	-0.533
17	14	15.5	15		16	13	14.5	14	359519.640	0.398
17	17	16.5	16		16	16	15.5	15	359519.640	0.043
17	18	15.5	15		16	17	14.5	14	359519.640	0.060
17	14	16.5	17		16	13	15.5	16	359519.640	-0.105
17	18	15.5	16		16	17	14.5	15	359522.170	0.336
17	17	15.5	16		16	16	14.5	15	359522.170	-0.053
17	16	17.5	18		16	15	16.5	17	359526.922	0.154
17	16	17.5	17		16	16	16.5	16	359526.922	0.105
17	18	16.5	16		16	17	15.5	15	359528.645	0.166
17	19	16.5	16		16	18	15.5	15	359530.907	-0.173
17	19	16.5	17		16	18	15.5	16	359532.351	0.032
17	15	16.5	16		16	14	15.5	15	359532.351	-0.478
17	17	16.5	17		16	16	15.5	16	359533.720	0.128
17	18	16.5	17		16	17	15.5	16	359536.394	0.396
17	15	16.5	17		16	14	15.5	16	359536.394	-0.383
17	17	17.5	17		16	17	16.5	16	359538.243	0.190
17	19	17.5	18		16	14	16.5	17	359538.243	-0.448
17	17	18.5	19		16	16	17.5	18	359539.686	0.476
17	15	17.5	17		16	18	16.5	16	359539.686	-0.424
17	17	18.5	18		16	16	17.5	17	359541.237	0.497
17	18	17.5	17		16	15	16.5	16	359544.462	-0.060
17	17	17.5	18		16	16	16.5	17	359547.914	-0.036
17	16	18.5	19		16	15	17.5	18	359550.079	0.398
17	18	17.5	18		16	17	16.5	17	359550.079	-0.296
17	19	17.5	17		16	14	16.5	16	359550.079	-0.483
17	16	18.5	18		16	15	17.5	17	359552.212	0.152
17	15	17.5	18		16	18	16.5	17	359554.795	0.010
17	18	18.5	18		16	17	17.5	17	359556.061	0.019

N^{\prime}	$J^{'}$	F_{1}^{\prime}	$F^{'}$	\leftarrow	N	J	F_1	F	v_{obs}	$v_{\rm obs-calc}$
17	20	18.5	18		16	19	17.5	17	359557.662	0.014
17	19	18.5	18		16	18	17.5	17	359559.121	0.312
17	17	19.5	19		16	16	18.5	18	359559.121	-0.475
17	18	18.5	19		16	17	17.5	18	359561.731	-0.094
17	17	19.5	20		16	16	18.5	19	359561.731	0.520
17	19	18.5	19		16	18	17.5	18	359561.731	-0.430
17	18	20.5	21		16	17	19.5	20	359564.975	0.348
17	18	20.5	20		16	17	19.5	19	359564.975	-0.195
17	20	19.5	19		16	19	18.5	18	359567.795	-0.103
17	20	19.5	20		16	19	18.5	19	359569.375	-0.090
17	19	19.5	19		16	18	18.5	18	359571.526	0.049
17	19	19.5	20		16	18	18.5	19	359573.748	-0.026
17	20	20.5	21		16	19	19.5	20	359573.748	-0.264
17	20	20.5	20		16	19	19.5	19	359573.748	0.499
17	19	21.5	22		16	18	20.5	21	359577.322	0.129
17	19	21.5	21		16	18	20.5	20	359577.322	0.210
17	19	20.5	21		16	18	19.5	20	359582.273	-0.064
17	19	20.5	20		16	18	19.5	19	359582.273	0.268
17	20	21.5	22		16	19	20.5	21	359587.540	0.256
17	20	21.5	21		16	19	20.5	20	359587.540	-0.102
17	20	22.5	23		16	19	21.5	22	359589.543	0.227
17	20	22.5	22		16	19	21.5	21	359589.543	-0.054
18	15	12.5	12		17	14	11.5	11	380597.403	-0.176
18	15	12.5	13		17	14	11.5	12	380599.372	0.332
18	15	13.5	13		17	14	12.5	12	380599.372	-0.309
18	15	14.5	14		17	14	13.5	13	380604.364	-0.073
18	15	13.5	14		17	14	12.5	13	380604.364	0.087
18	16	13.5	13		17	15	12.5	12	380608.327	0.439
18	16	13.5	14		17	15	12.5	13	380608.327	0.020
18	16	15.5	15		17	14	13.5	14	380612.289	0.212
18	15	14.5	15		17	15	14.5	14	380612.289	0.215
18	18	15.5	15		17	17	14.5	14	380624.962	0.113
18	18	15.5	16		17	17	14.5	15	380624.962	-0.060
18	15	15.5	16		17	14	14.5	15	380624.962	-0.072
18	17	16.5	17		17	16	15.5	16	380628.089	-0.183
18	17	17.5	18		17	16	16.5	17	380630.027	0.392
18	18	16.5	16		17	17	15.5	15	380630.027	-0.335
18	17	16.5	16		17	16	15.5	15	380631.588	0.062
18	17	17.5	17		17	16	16.5	16	380631.588	-0.019
18	15	17.5	18		17	14	16.5	17	380634.029	0.220
18	19	16.5	16		17	18	15.5	15	380634.029	-0.119
18	19	16.5	17		17	18	15.5	16	380636.677	0.367
18	18	16.5	17		17	17	15.5	16	380636.677	-0.276
18	17	18.5	19		17	16	17.5	18	380640.847	0.282
18	19	18.5	18		17	16	17.5	17	380640.847	0.213
18	19	17.5	17		17	18	16.5	16	380643.775	-0.045
18	18	17.5	18		17	17	16.5	17	380648.672	0.189
18	19	17.5	18		17	18	16.5	17	380650.954	0.319
18	16	17.5	18		17	15	16.5	17	380650.954	-0.369
18	18	19.5	20		17	17	18.5	19	380653.729	0.471
18	18	18.5	18		17	17	17.5	17	380653.729	-0.078
18	16	18.5	18		17	15	17.5	17	380653.729	-0.386
18	18	19.5	19		17	17	18.5	18	380653.729	-0.981
18	17	18.5	18		17	18	17.5	17	380659 740	0.159

Table 1 (continued)

$N^{'}$	$J^{'}$	F_{1}^{\prime}	$F^{'}$	\leftarrow	N	J	F_1	F	v _{obs}	$v_{\rm obs-calc}$
18	18	18.5	19		17	17	17.5	18	380662.507	-0.020
18	17	19.5	20		17	16	18.5	19	380664.554	0.527
18	19	18.5	19		17	18	17.5	18	380664.554	-0.352
18	19	20.5	20		17	18	19.5	19	380667 641	0.396
18	21	18.5	19		17	20	17.5	18	380667.641	0.135
18	16	18.5	19		17	15	17.5	18	380669 366	-0.078
18	20	10.5	19		17	19	18.5	18	380673 800	0.442
18	18	20.5	20		17	17	19.5	19	380673.800	-0.208
18	19	19.5	20		17	18	18.5	19	380676.056	-0.028
18	18	20.5	20		17	17	19.5	20	380676.056	0.502
18	20	19.5	20		17	19	18.5	19	380676.056	-0.418
18	19	21.5	20		17	18	20.5	21	380679 123	0.338
18	19	21.5	21		17	18	20.5	20	380670 123	-0.169
18	21	21.5	20		17	20	10.5	10	380681 006	-0.115
18	21	20.5	20		17	20	19.5	20	380683 565	-0.115
10	20	20.5	20		17	10	19.5	10	280685.505	-0.001
10	20	20.5	20		17	19	19.5	20	280687 700	0.014
10	20	20.5	21		17	20	19.5	20	380687.709	0.019
10	21	21.5	22		17	20	20.5	20	380687.709	-0.413
10	20	21.5	21		17	10	20.5	20	280601 422	0.125
10	20	22.5	23		17	19	21.5	22	280601.422	0.125
10	20	22.5	22		17	19	21.5	21	380695 920	-0.132
10	20	21.5	22		17	19	20.5	20	380695.920	-0.132
10	20	21.5	21		17	20	20.5	20	380093.920	0.237
10	21	22.5	23		17	20	21.5	22	280701.247	0.190
18	21	22.5	22		17	20	21.5	21	380703 528	0.165
18	21	23.5	23		17	20	22.5	23	380703 528	-0.074
19	16	13.5	13		18	15	12.5	12	401706 138	-0.117
19	16	13.5	14		18	15	12.5	13	401708 306	0.549
19	16	14.5	14		18	15	13.5	13	401708 306	-0.495
19	16	14.5	15		18	15	13.5	14	401713 761	0.375
19	16	15.5	15		18	15	14.5	14	401713 761	-0.234
19	17	14.5	14		18	16	13.5	13	401716 775	0.362
19	17	14.5	15		18	16	13.5	14	401716 775	-0.026
19	17	16.5	16		18	16	15.5	15	401721 856	0.473
19	16	15.5	16		18	15	14.5	15	401721 856	-0.109
19	17	15.5	16		18	16	14.5	15	401725 253	-0.023
19	17	15.5	15		18	16	14.5	14	401725.253	-0.773
19	16	16.5	16		18	15	15.5	15	401728.945	-0.365
19	17	16.5	17		18	16	15.5	16	401733.439	0.438
19	19	16.5	16		18	18	15.5	15	401733.439	0.207
19	19	16.5	17		18	18	15.5	16	401733.439	0.014
19	16	16.5	17		18	15	15.5	16	401733.439	-0.320
19	18	16.5	16		18	17	15.5	15	401733.439	-0.743
19	18	17.5	18		18	17	16.5	17	401735.872	-0.169
19	17	18.5	19		18	17	17.5	18	401737.219	0.259
19	18	18.5	18		18	17	17.5	17	401739.028	0.060
19	18	17.5	17		18	17	16.5	16	401739.028	-0.223
19	19	17.5	17		18	18	16.5	16	401739.028	-0.553
19	16	17.5	17		18	15	16.5	16	401741.624	0.206
19	16	18.5	19		18	15	17.5	18	401741.624	-0.300
19	20	17.5	18		18	19	16.5	17	401744.982	0.180
19	19	17.5	18		18	18	16.5	17	401744.982	-0.678
19	17	17.5	18		18	16	16.5	17	401746.545	-0.526

Table 1 (continued)

14010 1 ((commuted)									
N^{\prime}	$J^{'}$	F_{1}^{\prime}	$F^{'}$	<i>←</i>	N	J	F_1	F	v _{obs}	v _{obs-calc}
19	18	19.5	20		18	17	18.5	19	401748.738	0.345
19	20	19.5	19		18	19	18.5	18	401748.738	0.252
19	20	18.5	18		18	19	17.5	17	401753.346	0.278
19	21	18.5	18		18	20	17.5	17	401754.726	0.721
19	18	18.5	19		18	20	17.5	18	401754.726	-0.389
19	19	18.5	19		18	18	17.5	18	401757.209	-0.110
19	20	18.5	19		18	19	17.5	18	401759.604	0.321
19	21	18.5	19		18	16	17.5	18	401759.604	-0.293
19	19	20.5	21		18	18	19.5	20	401761.615	0.291
19	21	19.5	19		18	16	18.5	18	401761.615	-0.524
19	19	19.5	19		18	18	18.5	18	401763.403	0.043
19	18	19.5	19		18	17	18.5	18	401768.673	0.089
19	20	21.5	22		18	19	20.5	21	401774.343	0.117
19	17	19.5	19		18	20	18.5	18	401774.343	0.023
19	18	20.5	20		18	17	19.5	19	401774.343	-0.122
19	22	19.5	20		18	21	18.5	19	401776.034	0.115
19	17	19.5	20		18	16	18.5	19	401777.987	-0.149
19	20	20.5	20		18	19	19.5	19	401780.045	0.223
19	22	20.5	20		18	21	19.5	19	401780.045	-0.600
19	21	20.5	20		18	20	19.5	19	401782.373	0.451
19	19	21.5	21		18	18	20.5	20	401782.373	-0.061
19	20	20.5	21		18	19	19.5	20	401784.543	0.154
19	19	21.5	22		18	18	20.5	21	401784.543	0.634
19	21	20.5	21		18	20	19.5	20	401784.543	-0.294
19	20	22.5	23		18	19	21.5	22	401787.228	0.255
19	20	22.5	22		18	19	21.5	21	401787.228	-0.221
19	22	21.5	21		18	21	20.5	20	401790.289	-0.090
19	22	21.5	22		18	21	20.5	21	401791.809	-0.032
19	21	21.5	21		18	20	20.5	20	401793.727	-0.007
19	21	21.5	22		18	20	20.5	21	401795.878	0.181
19	22	22.5	23		18	21	21.5	22	401795.878	-0.404
19	22	22.5	22		18	21	21.5	21	401795.878	0.340
19	21	23.5	24		18	20	22.5	23	401799.546	0.094
19	21	23.5	23		18	20	22.5	22	401799.546	0.178
19	21	22.5	23		18	20	21.5	22	401803.717	-0.171
19	21	22.5	22		18	20	21.5	21	401803.717	0.264
19	22	23.5	24		18	21	22.5	23	401809.115	0.187
19	22	23.5	23		18	21	22.5	22	401809.115	0.008
19	22	24.5	25		18	21	23.5	24	401811.513	0.040
19	22	24.5	24		18	21	23.5	23	401811 513	-0.162
23	20	17.5	17		22	19	16.5	16	486074 110	-0.003
23	20	17.5	18		22	19	16.5	17	486076 108	0.540
23	20	18.5	18		22	19	17.5	17	486078 166	0.047
23	20	19.5	19		22	19	18.5	18	486084 661	0.024
23	20	19.5	20		22	20	19.5	19	486090 920	0.050
23	20	20.5	20		22	21	19.5	19	486100 372	0.438
23	22	22.5	23		22	20	21.5	22	486100 372	0 227
23	23	20.5	20		22	20	19.5	19	486100.372	0.093
23	23	20.5	20		22	22	10.5	20	486100.372	-0.140
23	23 21	20.5	21		22	20	20.5	20	486100.372	-0.453
23	21	21.5	22		22	20	20.5	21	486102 750	0.532
23	21	22.5	22		22	20	21.5	21	486104 103	0.332
23	22	21.5	21		22	$\frac{21}{22}$	20.5	20	486104.103	_0.071
23	23 20	21.3	21		22	10	20.5	20	400104.105	-0.9/1
23	20	21.5	21		22	19	20.5	20	480108.101	0.459

Table 1 (continued)

$N^{'}$	J'	F'_1	$F^{'}$	←	Ν	J	F_1	F	Vahs	Vobs-calc
23	20	22.5	23		22	10	21.5	22	486108 101	-0.060
23	20	22.5	23		22	19	21.5	22	486108.101	-0.000
23	20	22.5	22		22	19	21.5	21	486110 836	-0.384
23	24	21.5	21		22	23	20.5	20	486113 310	0.270
23	22	21.5	24		22	21	20.3	21	486113.310	-0.077
23	22	23.5	24		22	22	22.5	23	480113.310	-0.077
25	24	25.5	25		22	23	22.5	22	400115.510	-0.278
23	25	21.5	22		22	22	20.5	21	400115.510	-0.499
25	25	22.5	22		22	22	21.5	21	400119.042	0.202
23	24	22.5	25		22	21	21.5	22	400122.242	-0.034
23	24	22.5	22		22	23	21.5	21	400122.242	-0.023
23	23	22.5	22		22	24	21.5	21	480125.208	0.131
23	23	22.5	25		22	22	21.5	24	400123.200	-0.009
25	25	24.5	23		22	22	25.5	24	400127.727	0.303
23	21	22.5	25		22	25	21.5	22	480127.727	0.555
23	23	22.5	23		22	24	21.5	22	400127.727	-0.000
23	21	25.5	25		22	24	22.5	22	400127.727	-0.109
25	23	24.5	24		22	22	23.3	23	400127.727	-0.390
23	25	23.5	25		22	22	22.5	22	400155.972	0.244
23	23	23.5	23		22	21	22.5	22	400137.304	-0.324
25	25	23.5	24		22	23	22.5	23	400130.997	0.040
23	22	24.5	23		22	21	23.5	24	400130.997	-0.137
25	22	24.5	24		22	21	23.3	23	400141.172	0.380
23	23	25.5	24		22	24	22.5	25	400141.172	-0.217
25	24	23.5	23		22	25	24.5	24	400141.172	-0.300
23	21	23.5	24		22	23	22.5	23	400145.214	0.344
25	22	23.5	25		22	20	22.5	22	400145.214	-0.127
23	20	23.5	25		22	23	22.5	22	400145.214	-0.394
23	20	25.5	24		22	21	22.5	23	480140.078	-0.443
23	24	24.5	24		22	25	23.5	23	400147.970	-0.191
23	20	24.5	24		22	23	25.5	23	480147.970	-0.203
23	23	23.5	23		22	22	24.5	24	480149.993	0.307
23	25	24.5	24		22	24	23.5	23	400149.993	0.273
23	20	24.5	25		22	23	23.5	24	480149.995	-0.430
23	24	24.5	25		22	23	23.5	24	480151.002	0.273
23	23	23.5	20		22	22	24.5	23	480151.002	0.823
23	23	24.5	23		22	24	25.5	24	480151.002	-0.400
23	24	20.5	26		22	23	25.5	20	480153.099	-0.039
23	24	20.5	20		22	23	23.5	23	486155.099	-0.039
23	25	25.5	25		22	24	24.5	24	480100.085	-0.133
23	25	25.5	20		22	24	24.5	25	480102.287	0.473
23	20	20.5	26		22	25	25.5	20	486162.287	-0.418
23	20	20.5	20		22	23	25.5	23	480102.287	0.247
23	25	27.5	20		22	24	20.5	27	486165 860	0.120
23	25	21.5	27		22	24	20.5	20	480105.809	0.120
23 22	23 25	20.5	20 27		22	∠4 24	23.3 25.5	23 26	400109.133	-0.262
23 22	23	20.5	21		22	24 25	23.3 26.5	20 27	400109.133	-0.302
23 22	20	27.5	20 27		22	23 25	20.5	21	4001/4.330	-0.007
23 22	20	21.5	20		22	23 25	20.5	20	4001/4.330	-0.031
23 22	20	28.3 28.5	29 20		22	23 25	21.5	28 27	4801//.034	-0.127
23	20	28.3	28		22	25	27.5	21	4801//.034	-0.229

^a In MHz; for the v = 1 data set, please contact the authors.

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recorded, which lie in the frequency range 377-630 GHz. A total of 241 individual features were measured for the v = 1 state. This data set is available on request from the authors.

4. Analysis

The MnF data were fit to the following effective Hamiltonian, using a case $b_{\beta J}$ basis set [18]:

$$\dot{H}_{\rm eff} = \dot{H}_{\rm rot} + \dot{H}_{\rm sr} + \dot{H}_{\rm ss} + \dot{H}_{hf({\rm Mn})} + \dot{H}_{hf({\rm F})}$$
(1)

The terms in Eq. (1) describe rotational motion, spin-rotation and spin-spin fine structure and magnetic hyperfine interactions for the manganese and fluorine nuclei.

Due to the highly convoluted nature of the fine and hyperfine structure within each rotational transition of MnF, the spectral analysis was conducted in several stages. First, five clearly resolved features appearing on the high frequency side of the rotational transitions in the v = 0 level were fit to obtain preliminary values of B, D, the spin-spin constant λ , the spin-rotation constant γ , and the Mn hyperfine constants, $b_{\rm F}$ and c. From this initial fit, γ was found to have a positive value and λ a negative one, consistent with the signs of those constants obtained for MnH [7-9], lending some legitimacy to the analysis. Based on these preliminary parameters, the complete MnF spectrum was then repredicted. A simulation program was helpful in this regard. It was then immediately obvious that ¹⁹F hyperfine interactions had to be included in the analysis. (The strengths of some of the lines were clearly under-predicted and obvious doublets in the observed spectra were calculated to be single features.) Employing fluorine hf parameters eliminated many of these discrepancies, although it was found necessary to fix the dipolar constant of ¹⁹F to the value given in the matrix studies [14]. The data fit was again reiterated several times to 'fine tune' the observed line intensities and account for as many features in the experimental data as possible. For comparison, simulated spectra were generated.

The final results of the analysis are illustrated in Fig. 2. Here the observed spectrum of the $N = 18 \leftarrow 17$ transition (v = 0) near 380 GHz is pre-

sented in the top panel. In the lower panel, the simulated spectrum is shown, which is based on the constants established in the final fit, including relative intensities. All strong individual lines in these data are well reproduced by the simulation, as are many of the weaker features. (The simulation accounts for the second derivative spectrum and hence enables elimination of 'ghost' features.) Interestingly, the best fit included transitions with ΔJ changing by ± 2 and greater, as well as those with $\Delta F_1 = \pm 2$. These unusual transitions account for ${\sim}10\%$ of the observed lines. They arise from hyperfine mixing, which results in the breakdown of J as a good quantum number. Such effects were also noticed in MnH [7–9], another case where the hyperfine interactions were comparable to the spin splittings. The v = 1 data set was analyzed in an identical manner.

The spectroscopic parameters obtained for MnF (v = 0 and v = 1) are presented in Table 2. As shown in the table, in the final fit the dipolar hf constant for the ¹⁹F nucleus had to be fixed, as mentioned previously. All other spectroscopic constants are well determined, and the rms of the fits are 204 kHz (v = 0) and 244 kHz (v = 1). Curiously, the only spin parameters that were needed in the analysis were γ , the spin-rotation constant, and λ , the spin-spin parameter, and $\lambda_{\rm D}$. Centrifugal distortion corrections to γ , as well as higher order terms such as θ , γ_s , and b_s , were used in the initial analyses but could not be defined. In contrast, $\gamma_{\rm D}, \gamma_{\rm s}, \theta$, and $b_{\rm F_{\rm D}}$ were all found to be necessary to fit MnS[11] and MnO[10] in their $X^6\Sigma^+$ states.

One major difference between MnF and these other manganese compounds is the magnitude of the fine structure interactions, which is substantially smaller in the fluoride. For example, the spin-spin constant is near 10 GHz in MnS and 17 GHz in MnO, while in MnF it is -136.5 MHz – two orders of magnitude smaller. The spin-rotation constant is smaller by a factor of 4 in the fluoride relative to the sulfide and oxide as well, which both have $\gamma \simeq -71$ MHz [10,11]. Hence, higher order terms may be sufficiently small such that they are not needed for MnF. It also may be difficult to determine values of these higher-order constants as well, given the congested spectra. It is



MnF ($X^7\Sigma^+$: v = 0) N = 18 \leftarrow 17

Fig. 2. The observed spectrum of the $N = 18 \leftarrow 17$ transition of MnF (X⁷ Σ^+) near 380 GHz (top panel) and a simulated spectrum of the same transition, based on the constants in Table 2 determined in the fit (lower panel). The simulated spectrum reproduces the features in the actual data quite well, verifying the accuracy of the analysis. The measured spectrum is 140 MHz wide in frequency, and is an average of four scans, each ~ 1 min in duration.

Table 2 Spectroscopic parameters for MnF $(X^7\Sigma^+)^a$

Parameter	Millimeter-wave		Optical	Matrix ESR
	v = 0	v = 1	v = 0	
В	10582.60503(47)	10503.42888(38)	10545(21) ^b	
D	0.01383948(60)	0.01383454(31)		
γ	16.7152(30)	16.3554(36)		
λ	-136.511(96)	-142.3040(50)		
$\lambda_{\mathbf{D}}$	0.000927(40)	0.0000195(50)		
$b_{\rm F}({\rm Mn})$	413.615(30)	434.277(30)		442(6)° 443(6)°
c(Mn)	35.584(30)	25.005(30)		72(18) ^c , 48(18) ^c
$b_{\rm F}({\rm F})$	69.863(29)	72.40(19)		68(6) ^c , 75(6) ^c
$c(\mathbf{F})$	24 ^d	24 ^d		24(18) ^c , 30(18) ^c
rms	0.204	0.244		
Be	10622.19311(60)			
α _e	79.1762(12)			

 a In MHz; errors are 3σ and apply to the last quoted decimal places. b From [15]. Values originally quoted in cm $^{-1}$.

^c From [14], neon matrix is first value, argon matrix is second value.

^d Held fixed (see text).

interesting to note that the electric quadrupole constant eqQ for the ⁵⁵Mn nucleus was not defined in the MnF analysis as well; again, this parameter was determined for both MnO and MnS. For the latter species, however, lower N rotational transitions were recorded, and quadrupole splittings decrease with increasing N. Moreover, these spectra were far less congested.

Also included in Table 2 are the constants determined for MnF from previous work. The data set is small: it includes a gas-phase estimate of the rotational constant (v = 0) from optical spectra [15], as well as hf parameters from matrix ESR studies [14]. The values for the rotational constant B are in reasonable agreement. The hf parameters $b_{\rm F}$ and c compare satisfactorily, as well, for both ¹⁹F and ⁵⁵Mn nuclei ($c(^{19}F)$) was fixed, as mentioned). It is also not clear whether the uncertainties of the matrix values quoted from [14] are one or three standard deviations. If they are only 1σ , then the gas-phase and matrix isolation constants are in complete agreement. If the quoted uncertainties are 3σ , then the gas-phase parameters are systematically smaller than the matrix values for the ⁵⁵Mn nucleus. This systematic difference was found in MnH, where the Fermi contact term for the 55Mn nucleus was 11% smaller, based on the gas-phase study. This effect was attributed to a large matrix shift.

5. Discussion

5.1. Minimal fine structure interactions in MnF

In comparison to molecules in equally high spin states such as MnS(${}^{6}\Sigma^{+}$) and MnO(${}^{6}\Sigma^{+}$), the spin–spin constant determined for MnF is remarkably small. A similar situation is found in MnH(X⁷ Σ^{+}), where $\lambda = -97$ MHz [9], comparable to that found for MnF. The small value of λ can be understood in terms of second-order contributions to this parameter. The magnitude of λ is determined by the pure microscopic spin–spin interactions, and a second-order spin–orbit perturbation [19], i.e.,

$$\lambda = \lambda^{\rm ss} + \lambda^{\rm so}.\tag{2}$$

The latter effect is thought to dominate in heavier molecules, and certainly those containing a 3d transition metal. The spin–orbit contribution arises from perturbations of nearby excited states, following the selection rules $\Delta S = 0 \pm 1$; $\Delta \Omega = 0$; $\Sigma^{\pm} \leftrightarrow \Sigma^{\mp}$ [19]. Consequently, a $^{7}\Sigma^{+}$ state can only interact with $^{7}\Sigma^{-}$, $^{5}\Sigma^{-}$, $^{5}\Pi$, and $^{7}\Pi$ states for this type of coupling.

Little is quantitatively known about the excited electronic states of MnF, other than the $A^7\Pi$ state lies 28 000 cm⁻¹ higher in energy above the $X^7\Sigma^+$ state [15]. There is some indication that the $a^5\Sigma^+$ may lie lower in energy than the A state [20], and the $b^5\Pi$ term as well [16,9]. However, no theoretical calculation exists for MnF to verify these energies. The $a\Sigma^+$ state has positive Kronig symmetry and hence cannot interact with the $X^7\Sigma^+$ via second-order spin–orbit coupling. The $b^5\Pi$ term is also eliminated as a possible perturber because it arises from a 3d⁶ electron configuration, as opposed to 3d⁵. The only remaining perturber is the $A^7\Pi$ state. The second order spin-orbit interaction for MnF is therefore well approximated by the expression

$$\lambda^{\rm so} \cong \frac{|\langle \mathbf{A}^7 \Pi | \hat{H}_{\rm so} | \mathbf{X}^7 \Sigma^+ \rangle|^2}{E(\mathbf{X}^7 \Sigma^+) - E(\mathbf{A}^7 \Pi)} \tag{3}$$

The structure of MnF is likely to be highly ionic. Thus, the $X^7\Sigma$ and $A^7\Pi$ states can be approximated as Mn⁺ (3d⁵4s¹) F⁻ (2p⁶) and Mn⁺ (3d⁵4p¹) F⁻ (2p⁶). \hat{H}_{so} is a one electron operator and diagonal in ℓ . Consequently, at least to first order, the $X^7\Sigma$ and $A^7\Pi$ states cannot connect via this interaction. The numerator in the above expression must be negligible. The large energy difference in the denominator (28 000 cm⁻¹) also reduces the value of λ^{so} .

The magnitude of the spin-rotation constant in MnF is also small ($\gamma = 16.7152$ MHz). Again, there are two main contributions to this parameter: microscopic electron spin-nuclear rotation coupling and a second-order spin-orbit effect [19]. The latter interaction involves the cross-term $\hat{H}_{so} \times \hat{H}_{rot}$ and follows the selection rule $\Delta S = 0$; hence, once again, the $A^7\Pi$ state is the main perturber. As previously discussed, \hat{H}_{so} cannot readily connect these two states; they have a large energy separation as well. The second-order contribution to γ is therefore minimal. In comparison, the spinrotation constant in MnH is significantly larger ($\gamma = 909.6$ MHz [9]). This increase reflects the larger rotational constant in the hydride, which enters into γ through \hat{H}_{rot} .

5.2. Comparison of hyperfine parameters

Trends across the periodic table for 3d metal oxides have been examined in detail [e.g. 1,21,22], including numerous calculations concerning the bonding and degree of hybridization of molecular orbitals. For the fluoride analogs, such studies are far more incomplete. On the other hand, such trends can be examined in 3d fluorides by comparison of ¹⁹F magnetic *hf* constants, which give insight into the nature of the molecular orbitals of the species. Unfortunately, such *hf* parameters have only been determined for a few of the 3d fluorides; these values are given in Table 3 for TiF, FeF and MnF. (NiF is not included in this group because only h = [a + (b + c)/2] could be established [23].)

As shown in Table 3, the Fermi contact term $b_{\rm F}$ for the fluoride nucleus for all three species is relatively small, indicating that the unpaired electrons from s atomic orbitals in these radicals are primarily located on the metal atom. This result is not surprising because these species are predominantly ionic and hence exhibit an M⁺F⁻ structure. Thus, there are no unpaired electrons present directly on the ¹⁹F nucleus in this picture. The differences in the magnitudes of the $b_{\rm F}$ parameters in these species, however, can be best rationalized in terms of their proposed electron configuration, shown in Table 3. The possible contributing electrons to the Fermi contact interaction are the 9 σ and 10 σ orbitals. The 9 σ is considered to be primarily non-bonding, hence it resides exclusively on the metal atom [21]. The 10σ orbital is antibonding and likely consists of some combination of fluorine p_{σ} and metal sd_{σ} atomic character. It is likely that the electron in the 10σ orbital makes the primary contribution to $b_{\rm F}$ in MnF and FeF; their constants are closer in magnitude. TiF has no electrons in the 10σ orbital; consequently, the value of $b_{\rm F}$ in this species is smaller.

The dipolar constant c in all three species is also small in magnitude. Again, because the unpaired electrons are primarily located on the metal atom, their contribution to c is negligible. The dipolar constant in FeF is significantly larger than in TiF; this increase likely arises because of occupation of the 10σ orbital.

The ¹⁹F *hf* constants can thus be interpreted as resulting from unpaired electrons that are primarily located on the 3d metal. Such a picture is also borne out in the values of the Mn *hf* constants. For MnF, $b_F = 413.61$ MHz – a factor of 10 larger than that for the fluorine nucleus. In fact, on formation of MnF, 55% of the 4s character is retained, in comparison with Mn⁺. ($A_{iso}(Mn^+) =$ 770 MHz [24].) This result suggests that MnF is highly ionic, basically Mn⁺F⁻.

Large manganese Fermi contact parameters are found for many diatomic manganese species. As shown in Table 4, b_F falls in the range from 206.5 MHz for MnS [11] to 479.9 MHz in MnO [10]. The dipolar *c* constant is correspondingly small. As the table also illustrates, b_F decreases from MnO to MnS (479.9 vs 206.5 MHz), and from MnF to MnCl as well (413.6 vs 376 MHz). Such a trend suggests a decrease in ionicity as the columns of the periodic table are descended. Based on the b_F values, MnH and MnS appear to be the most covalent of these compounds. One might expect

Table 3					
¹⁹ F hyperfine	parameters	for	transition	metal	fluorides ^a

Molecule	а	$b_{ m F}$	С	Configuration	Reference
$\begin{array}{l} TiF(X^{4}\Phi_{r})\\ MnF(X^{7}\Sigma^{+})\\ FeF(X^{6}\Delta_{i}) \end{array}$	67.4(1.1) - -0.45 ^b	41(14) 69.863(29) 91.7(3.7)	-28(14) 24 ^b 51.7(3.5)	$\begin{array}{l} 9\sigma^{1}1\delta^{1}4\pi^{1} \\ 9\sigma^{1}1\delta^{2}4\pi^{2}10\sigma^{1} \\ 9\sigma^{1}1\delta^{3}4\pi^{2}10\sigma^{1} \end{array}$	[5] This work [28]

^a In MHz; errors are 3σ and apply to the last quoted decimal places.

^b Held fixed (see text).

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Molecule	Ground state	$b_{ m F}$	С	Reference							
MnH	$^{7}\Sigma^{+}$	279(1)	36.0(2.4)	[8]							
MnF	$^{7}\Sigma^{+}$	413.615(30)	35.584(30)	This work							
MnCl	$^{7}\Sigma^{+}$	376(11)	-102(30)	[30]							
MnO	$^6\Sigma^+$	479.861(100)	-48.199(178)	[10]							
MnS	$^6\Sigma^+$	206.51(79)	-27.8(1.6)	[11]							

Table 4 Hyperfine parameters for manganese diatomics^a

^a In MHz; errors are 3σ and apply to the last quoted decimal places.

MnF to be the most ionic, based on electronegativity arguments. In contrast, the $b_{\rm F}$ constants indicate that MnO has the highest degree of ionic character, a likely result of the contribution of the Mn²⁺O²⁻ structure.

5.3. Further trends in 3d metal flourides

The 3d metal fluorides are thought to be predominantly ionic in character. Certainly MnH is less ionic than MnF, based on comparison of $b_{\rm F}$ values. On the other hand, there may be a small increase in covalency across the 3d row. For example, Boldyrev and Simons [25] suggest that titanium carries only +0.82 charge in TiF. In contrast, Pouilly et al. [26] calculate that FeF is intermediate in its bonding character; 65% of the structure for iron fluoride is predicted to be ionic; the rest is thought to be covalent. No such calculations exist for MnF, so a direct comparison is difficult.

Some insight into the bonding in MnF can perhaps be gained by considering the trend in bond lengths. Of all 3d transition metal fluorides, MnF has the longest bond distance, $r_0 = 1.839$ Å (and $r_e = 1.836$ Å), with TiF having the second longest one ($r_0 = 1.834$ Å [5]). CrF has a significantly shorter distance of $r_0 = 1.788$ Å, as does FeF(1.784 Å) [27,28]. Core contraction alone would suggest that the bond distances should steadily decrease across the 3d row [1]. Clearly they do not.

Although the fluorides are chiefly ionic compounds, the abrupt increase in bond length at MnF can be understood in terms of a molecular orbital picture. The electron configuration in CrF is likely to be $9\sigma^1 \ 1\delta^2 \ 4\pi^2$. Another electron is added to the orbitals in the formation of MnF, in this case the 10σ antibonding orbital. This addition should increase the bond length, as it does. In FeF, the next electron adds to the 1δ orbital, which is completely nonbonding and does little to influence the bond distance. Core contraction causes the bond length in FeF to shorten. An identical situation is observed in the 3d transition metal oxides [1,21]. Another comparison of note is the bond length in MnF relative to MnO. For the oxide, $r_0 = 1.648$ Å [10], as opposed to 1.839 Å. The 0.2 Å difference can be explained if MnO has partial Mn²⁺O²⁻ character (MnF can only be Mn^+F^-); it also can be attributed to a higher bond order in MnO, as is found in TiO [29]. Hence, it is likely that some combination of ionic and covalent effects is influencing the behavior of these transition metal compounds.

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