Hyperfine Structure of the MnH X 7-Sigma(+) State: A Large Gas-to-Matrix Shift in the Fermi Contact Interaction

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Hyperfine structure of the MnH \( X \, ^7\Sigma^+ \) state: A large gas-to-matrix shift in the Fermi contact interaction

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Sub-Doppler spectra of the \( A \, ^7\Pi - X \, ^7\Sigma^+ \) (0,0) band of gas phase MnH near 5680 Å were recorded by intermodulated fluorescence spectroscopy. The spectra reveal hyperfine splittings arising from both the \( ^{55}\text{Mn} \) and \( ^1\text{H} \) nuclear spins. Internal hyperfine perturbations have been observed between the different spin components of the ground state at low \( N^\prime \). From a preliminary analysis of several rotational lines originating from the isolated and unperturbed \( F_s (J^\prime = 3) \) spin component of the \( X \, ^7\Sigma^+ \, (N^\prime = 0) \) level, the \( ^{55}\text{Mn} \) Fermi contact interaction in the ground state has been measured as \( b_F = A_{iso} = 276(1) \) MHz. This value is 11% smaller than the value obtained by Weltner et al. from an electron-nuclear double resonance (ENDOR) study of MnH in an argon matrix at 4 K. This unprecedented gas-to-matrix shift in the Fermi contact parameter is discussed.

I. INTRODUCTION

The \( A \, ^7\Pi - X \, ^7\Sigma^+ \) (0,0) band of MnH, near 5680 Å, was first observed in emission and absorption by Heimer in 1936.1 Six years later Nevin performed a pioneering rotational analysis of this very complex system—at that time an enormously difficult task, considering that there are 147 rotational branches allowed in a \( ^7\Pi - ^7\Sigma \) transition in the Hund’s case (a)—case (b) limit, of which he succeeded in identifying 49.2 Using higher resolution, we have extended Nevin’s rotational analysis by identifying nearly 100 new branches, including many obeying the unusual selection rule \( \Delta J = \pm 2 \). These latter are hyperfine-induced, rotationally forbidden \( O \) and \( S \) branches, which are surprisingly strong at low \( J \); they arise from the strong mixing of the \( X \, ^7\Sigma^+ \) electron spin components by the manganese hyperfine interactions, which destroy the “goodness” of \( J \) as a quantum number in the ground state. These observations will be reported in detail elsewhere.3

Our original interest in the \( A - X \) system of MnH was to see what information the hyperfine structure caused by the \( ^{55}\text{Mn} \) nucleus gives about the bonding in a system such as MnH. An immediately obvious, and very striking, observation concerns the \( X \, ^7\Sigma^+ \) ground state: Welter and co-workers,4 in their electron-nuclear double resonance (ENDOR) work on MnH in an argon matrix at 4 K, determined the value \( A_{iso} = b_F = 310.8(7) \) MHz for the manganese Fermi contact parameter in the \( X \, ^7\Sigma^+ \) ground state; the present gas-phase work gives \( b_F = 276(1) \) MHz, which is 11% below the matrix value. This unexpectedly large gas-to-matrix shift is discussed briefly.

II. EXPERIMENTAL

Our hollow cathode sputter source for producing transition metal diatomic molecules, based on a design by Trkula et al.,5 has been described elsewhere.6 MnH molecules, formed in an argon dc discharge above a manganese-impregnated copper hollow cathode, flow through a \( 15 \times 2 \) mm slit into a chamber pumped to ~1 Torr. Sub-Doppler spectra of MnH were recorded using the technique of intermodulated fluorescence (IMF).7 The output from a Coherent 699-29 ring dye laser, operating with either Rhodamine 6G or 110 (Exciton), was separated into two beams, each of ~100 mW intensity. The two beams were mechanically chopped at 240 and 360 Hz, focused with 1 m focal length lenses to approximately 1 mm in diameter over a 10 cm length, counterpropagated through the vacuum chamber, and overlapped 1 cm above the slit in the center of the molecular flow. \( A - X \) (0,0) fluorescence at the laser wavelength was detected through an appropriately chosen 10 nm bandpass interference filter. The Doppler-limited signal was monitored by a lock-in amplifier referenced at 360 Hz, while the sub-Doppler signal was detected at the 600 Hz sum frequency with a second lock-in (Stanford Research SR510). The spectra were calibrated by simultaneously recording the \( I_2 \) fluorescence excitation spectrum.8

III. ANALYSIS OF THE HYPERFINE STRUCTURE

For the MnH \( X \, ^7\Sigma^+ \) state, where the electron spin splitting is larger than the hyperfine splitting, a case (b) coupling scheme for the two spinning nuclei most closely approximates the observed energy level patterns. In this coupling scheme, we have

\[
N + S = J; \quad J + I_1 = F_1; \quad F_1 + I_2 = F;
\]

with basis functions \(|NASI_1F_1I_2F\rangle\). We associate \( I_1 \) with the \( ^{55}\text{Mn} \) nuclear spin \((I = \frac{3}{2})\) and \( I_2 \) with the \( ^1\text{H} \) spin \((I = \frac{1}{2})\), because the observed manganese contribution to the hyperfine splitting is much larger than that arising from the proton spin.

The hyperfine Hamiltonian for a diatomic molecule with the two nonzero nuclear spins in a \( \Sigma \) state may be writ-
ten
\[ H_{\text{SN}} = b^{(1)} I_0 \cdot S + c^{(1)} I_0 S_z + b^{(2)} I_2 \cdot S + c^{(2)} I_2 S_z. \]  
(1)

The nuclear spin-rotation \((c_e)\) and electric quadrupole \((eQg)\) interactions have been neglected in this analysis of the ground state.

The Hamiltonian can also be expressed in terms of the Fermi contact parameter \(b_F = b + i c\) as
\[ H_{\text{SN}} = b_F^{(1)} I_0 \cdot S + c^{(1)} (I_0 S_z - i I_0 \cdot S) + b_F^{(2)} I_2 \cdot S 
+ c^{(2)} (I_2 S_z - i I_2 \cdot S), \]
where \(b_F^{(1)}\) is proportional to the unperturbed electron spin density at the nucleus \(i\),
\[ b_F^{(1)} = \frac{8\pi}{3} g_{\mu_B} g_S \mu_N |\Psi(r = 0)|^2. \]

Matrix elements of the hyperfine Hamiltonian in a case \((b_{12})\) basis have been calculated by Ryzlewicz et al.\(^9\) using spherical tensor notation. The formulas are lengthy and are not listed here. It is important to note that the Fermi contact term for \(I_0 \cdot S\) is diagonal in \(N\) and \(F_i\), but also contains matrix elements off diagonal in \(J\). Thus for a particular value of \(N\), there exist \(\Delta J = \pm 1\) hyperfine matrix elements which connect the various spin components belonging to that \(N\) value. If spin components differing in \(J\) by one lie

\[
\langle NSJ_i F_1 F \mid b F_1 I_0 \cdot S \mid NSJ_i F_1 F \rangle
\]
\[ = \frac{F_1 (F_1 + 1) - 1}{4 J (J + 1)} \[ - b_F^{(2)} (N(N + 1) - J (J + 1) - S(S + 1)) \rangle. \]

(2)

For the \(X^2 \Sigma^+\) \(N = 0\) level, with \(J = 3, S = 3\), and \(I_1 = 1\), this formula simplifies to
\[ \langle H_{\text{SN}} \rangle = 2 b_F^{(1)} [ F_1 (F_1 + 1) - 2]. \]  
(3)

The \(F_1 (F_1 + 1)\) dependence of this diagonal matrix element produces the familiar Landé pattern spacing for the manganese hyperfine structure.

When the \(^1\)H nuclear spin is included, every Mn hyperfine level is doubled. For the \(N = 0, J = 3\) rotational level of MnH, where \(F_i (Mn)\) ranges from \(5\) to \(1\), there are 12 energy levels, with the total angular momentum \(F\) ranging from 6 down to 0 (see Fig. 1). Pairs of hyperfine levels with the same value of \(F\) [with \(F_i (Mn)\) differing by 1] interact through the \(^1\)H Fermi contact matrix elements. However, taking the ground state value for the proton Fermi contact parameter from Ref. 4, \(b_F^{(2)} = b^{(2)} + i c^{(2)} = 6.79 (3) \text{ MHz}\), we calculate the energy shifts caused by these off-diagonal \(^1\)H matrix elements to be less than 1 MHz, and therefore we do not include them.

We have recorded sub-Doppler spectra of seven transitions originating from the rotational level \(X^2 \Sigma^+, N = 0, F_i\). The sub-Doppler spectrum of the \(^1R_{21} (0)\) transition at \(17 \pm 0.65 \text{ cm}^{-1}\) is illustrated in Fig. 1. In this spectrum, the 12 strong \(\Delta F = \Delta J\) transitions are supplemented by weaker close together, then these matrix elements can cause internal hyperfine perturbations, as first observed by Richards and Barrow in the \(X^2 \Sigma^-\) state of VO.\(^10\) For the \(MnH X^2 \Sigma^+\) state, these elements have the effect of destroying the "goodness" of \(J\) as a quantum number at low \(N\), where the hyperfine interactions are larger than the electron spin splittings. As evidence of this, we observe hyperfine-induced \(\Delta J = \pm 2\) \((O\) and \(S)\) branches in the Doppler-limited spectrum of the \(A^3 \Pi - X^2 \Sigma^+\) \((0,0)\) band.

In this preliminary analysis of the ground state hyperfine structure, we note that the \(X^2 \Sigma^+, N = 0\) level is unique in having only one electron spin component, namely \(F_i (J = 3)\).\(^11\) The \(^55\)Mn Fermi contact interaction, being diagonal in \(N\), cannot connect the \(F_i (N = 0)\) level to any other rotational level. The diagonal matrix elements of the dipolar interaction \((I_0, S_z - i I_0 \cdot S)\) and the manganese quadrupole Hamiltonian are zero in the \(F_i (N = 0)\) level, but although they do have elements of the type \(\Delta N = \pm 2\), the \(N = 2\) levels lie \(BN(N + 1) \approx 30 \text{ cm}^{-1}\) away, so that their effects are negligible. Thus the manganese hyperfine structure of the single \(F_i (J = 3)\) spin component of \(N = 0\) will be very accurately described by the diagonal elements of the Fermi contact Hamiltonian \(b F_1 I_0 \cdot S\). To calculate these elements, we set \(J = J'\) in the formulas of Ref. 9 and evaluate the diagonal \(^55\)Mn hyperfine matrix element as

\[ \Delta F \neq \Delta J \] transitions, along with their associated crossover resonances, which are characteristic artifacts of the IMF scheme.\(^12\) These \(\Delta F \neq \Delta J\) transitions, which occur with greatest intensity at low \(N\), are particularly useful, for they provide direct measures of the upper and lower state hyperfine combination differences. From the seven \(N^* = 0\) transitions for which we have recorded sub-Doppler spectra, 35 measurements of ground state combination differences were made. These are listed in Table I, where the measurements with larger uncertainty, arising from weak or blended features, have been denoted. These measurements were assigned reduced weights in the least-squares fit.

The \(N^* = 0\) hyperfine combination differences were fitted to the energy level expression derived above [Eq. (3)]. Although this expression involves only the \(X^2 \Sigma^+\) manganese Fermi contact parameter, the experimental combination differences also carry information about the hydrogen hyperfine coupling constants. However, the \(^1\)H splitting in the ground state may safely be neglected because the Fermi contact parameter for the proton is so small. With \(b_F^{(2)} = 7 \text{ MHz}\), we calculated that the variation of the \(^1\)H doubling for consecutive values of \(F_i\) for the \(N^* = 0\) level would be at most 6 MHz. For example, the \(F^* = 5 - F^* = 6\) hydrogen doubling for \(F^*_i = S_i^1\) (see Fig. 1) is calculated to be only 3
MHz larger than the $F'' = 4 - F'' = 5$ hydrogen doubling for $F'' = 4.5$. Thus the difference between the $F'' = F'' - 0.5$ and $F'' + 0.5$ combination differences is negligible; the present measurements would only be sensitive to a ground state $b_f^{(2)} \approx 30$ MHz. The fitted value for the ground state $^{55}$Mn Fermi contact parameter is $b_f^{(1)} = 276(1)$ MHz, which is 11% smaller than the argon matrix value of 310.8(7) MHz.4

In order to understand the upper state hyperfine structure, a more detailed analysis of sub-Doppler spectra involving all seven $^{4}$TII spin components is required. The $A^{7}$TII state, where spin uncoupling has appreciably mixed the seven spin components even at low values of $J$, is in a coupling case intermediate between Hund's case (a) and (b); therefore, the hyperfine structure cannot be treated using a simple limiting-case analysis as has been done here for the ground state.13

IV. CONCLUSIONS

For a limited number of diatomic molecules, the hyperfine interaction has been measured both in the gas phase and for molecules isolated in an inert gas matrix.14 For such molecules, it is observed that the gas-to-matrix shift in the value of $b_F$ is very small, generally less than a few percent. CN appears to be the only exception, where the Ar matrix value for $b_F^{(14)N}$ is 10% smaller in absolute magnitude than the value obtained from gas phase electron spin resonance (ESR).15 However, Weltner has pointed out that the unusually small size of the Fermi contact parameter for CN [in the gas phase, $b_F^{(14)N} = -12$ MHz] may serve to magnify anomalously the percentage change in going from the gas phase to the matrix.15 In BaF, the $b_F$ value for $^{137}$Ba is 4% smaller in the gas phase than in a neon matrix,16 a shift in the same direction as in MnH, but smaller in size. Clearly
TABLE I. MnH $X^1\Sigma^+ - F_1 (N = 0, J = 3)$ hyperfine combination differences (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency (cm$^{-1}$)</th>
<th>$F_i (5\bar{i} - 4\bar{j})$</th>
<th>$F_i (4\bar{i} - 3\bar{j})$</th>
<th>$F_i (3\bar{i} - 2\bar{j})$</th>
<th>$F_i (2\bar{i} - 1\bar{j})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1(0)$</td>
<td>17 568.46</td>
<td>0.0519*</td>
<td>0.0514*</td>
<td>0.0424*</td>
<td>0.0423</td>
</tr>
<tr>
<td>$Q_1(0)$</td>
<td>17 589.65</td>
<td>0.0519</td>
<td>0.0509*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3P_{1/2}(0)$</td>
<td>17 644.23</td>
<td>0.0513*</td>
<td>0.0505</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3Q_{1/2}(0)$</td>
<td>17 666.00</td>
<td>0.0517*</td>
<td>0.0502</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3R_{1/2}(0)$</td>
<td>17 694.64</td>
<td>0.0496*</td>
<td>0.0505*</td>
<td>0.408</td>
<td>0.0404*</td>
</tr>
<tr>
<td>$^3Q_{3/2}(0)$</td>
<td>17 731.66</td>
<td>0.0510</td>
<td>0.0508</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3R_{3/2}(0)$</td>
<td>17 810.71</td>
<td>0.0501</td>
<td>0.0501</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated combination differences: 0.0506, 0.0414, 0.0322, 0.0230.

$^*$Datum deweighted by a factor of 4 in the fit due to lower signal-to-noise or a blending of lines. The notation for the rotational assignment is standard $\Delta J = \Delta m_J (N^*)$, where $a$ and $b$ indicate the upper and lower state spin components, respectively. The headings above the vertical columns of hyperfine combination differences indicate the values of $F_i$ and of $F$ which uniquely identify the two levels involved. For example, the leftmost column lists the energy difference $E(F_i = 5\bar{i}, F = 6) - E(F_i = 4\bar{j}, F = 5)$ in wave numbers. For $Q$ lines ($\Delta J = 0$), where two measurements of the same combination difference are possible, the $R - Q$ combination difference (where $R$ and $Q$ denote $\Delta F = 1$ and $\Delta F = 0$) is listed above the $Q - P$ combination difference. Derived Fermi contact parameter $b_F^{(1)} = 0.00920(21)\text{ cm}^{-1} = 276(1)\text{ MHz}$, with 1σ uncertainty in parentheses. Standard deviation of the fit = 0.00072 cm$^{-1}$.

then, the 11% gas-to-matrix shift in $b_F^{(1)}$ for MnH is surprisingly large.

If one considers MnH to be predominantly ionic (the ionic-covalent curve crossing radius is 2.16 Å, which is 25% larger than the equilibrium bond length $r_e = 1.73$ Å), the electronic configurations of the ions are Mn$^+$ (3$d^4$4$s^1$) and H$^-$ (1$s^2$). The derived $^{55}$Mn hyperfine parameter $b_F^{(1)}$ is directly proportional to the unpaired electron spin density at the manganese nucleus

$$b_F^{(1)} = \frac{8\pi}{3} g_\mu_B g_N \mu_N |\Psi(r = 0)|^2.$$ 

Since only s electrons have nonzero amplitude at $r = 0$, it is the Mn 4s electron which gives rise to the observed Fermi contact interaction. However, the electric field of the H$^-$ ion in the molecule polarizes the Mn$^+$ ion by mixing in Mn 4p. An approximate determination of the 4s character in this $sp$ hybridized orbital can be made by comparing the molecular Fermi contact interaction $b_F^{(1)}$ (MnH $X^1\Sigma^+$ = 276 MHz to that of the free Mn$^+$ ion $b_F^{(Mn^+)} = 770$ MHz). One then finds the effective fraction of a 4s electron to be 276/770 = 36% for MnH in the gas phase. This may be compared with 40% Mn 4s determined for MnH trapped in an argon matrix.

This polarization of the manganese ion via $sp$ hybridization shifts electron density out beyond the manganese nucleus and away from the anion, with the accompanying effect of reducing the molecular dipole moment, because the dipole induced at the manganese ion counteracts the Mn$^+$ H$^-$ dipole moment. An argon matrix, being a dielectric medium, should stabilize larger dipole moments and drive polarization in guest molecules in that direction. This is precisely what is observed for MnH, where the polarization of the 4s valence electron by the H$^-$ anion is reduced in going from the gas phase to the argon matrix. This model also qualitatively explains the $^{137}$BaF results, where the $p$ and $d$ hybridization of the lone 6s electron on the metal center is diminished by the neon matrix. Thus the large gas-to-matrix shift in the Fermi contact parameter for MnH can be understood in terms of the polarizing influence of the argon host.

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1T. Heimer, Naturwiss. 24, 521 (1936).
9C. Rydzewicz, H.-U. Schütte-Pahlmann, J. Hoft, and T. Törnring, Chem. Phys. 71, 389 (1982). Table 1 should be corrected by replacing the reduced matrix element of $I_{05} (I_{05} || I_{05} || I_{05})$ with that of $I_{05} (I_{05} || I_{05} || I_{05})$ in the formula given for the Fermi contact matrix element for nucleus 1.
11In standard spectroscopic notation, the symbol "F_1" has two meanings. We use Roman type F_1 to denote the J = N + 3/2 spin component of the ground state and italic F_1 to denote the quantum number which results from the coupling of J and I_1.