Hyperfine Structure and Stark Effect in the $[18.0]4 - X^3\Phi_4$ Transition of Iridium Hydride, IrH and $[18.2]4 - X^3\Phi_4$ Transition of Iridium Deuteride, IrD

C. Linton^{a,*}, A. D. Granger^b, A.G. Adam^b, T. C. Steimle^c

^a Centre for Laser, Atomic, and Molecular Sciences and Physics Department

University of New Brunswick, 8 Bailey Drive, Fredericton, NB, Canada E3B 5A3

^b Centre for Laser, Atomic, and Molecular Sciences and Chemistry Department,

University of New Brunswick, 30 Dineen Drive, Fredericton, NB, Canada E3B 5A3

^c Department of Chemistry and Biochemistry ,Arizona State University, Tempe, AZ

85287-1604, USA

* Corresponding author: Dr. C. Linton, Physics Department, University of New Brunswick,

8 Bailey Drive, Fredericton, NB, Canada E3B 5A3

Phone: 1-506-458-7954. Fax: 1-506- 453- 4581

Email: colinton@unb.ca

Abstract

High resolution spectra of IrH and IrD, with full width at half maximum (FWHM) of $\sim 0.001 \text{ cm}^{-1}$, have shown well resolved hyperfine structure due to the nuclear spin, $I = 3/2$, of ^{193}Ir and ^{191}Ir . Analysis of the hyperfine structure in the $[18.2]4 - X^3\Phi_4$ transition of ^{193}IrD and ^{191}IrD yielded well defined magnetic and quadrupole Ir hyperfine parameters which showed that the ground $X^3\Phi_4$ state originates predominantly from the two open-shell $\text{Ir}(5d\pi^3 5d\delta^3)$ configuration with a significant contribution from the four open-shell $\text{Ir}(5d\sigma 5d\pi^3 5d\delta^3 6s\sigma)$ configuration. Examination of the Stark effect in the $[18.0]4 - X^3\Phi_4$ transition of ^{193}IrH yielded electric dipole moments of 1.23(1) D and 0.76(1) D for the ground and excited states, respectively. The hyperfine constants and the dipole moment of the ground state are seen to follow the trend shown by the isovalent molecules, CoF, CoH and IrF.

Keywords:

Laser-induced fluorescence

Hyperfine structure

Stark Effect

Dipole Moment

Electron configuration

Iridium hydride and deuteride

1. Introduction:

In a recent publication [1], we reported the first observation and rotational analysis of pulsed laser induced fluorescence (LIF) spectra of IrH and IrD, at medium resolution (FWHM $\sim 0.35\text{ cm}^{-1}$), using the laser ablation source at the University of New Brunswick (UNB). Because of the large rotational constant, B, the rotational structure was well resolved but limited to low J lines (up to J $\sim$ 9). Transitions to eight excited states from the ground state were observed for both the hydride and deuteride. Rotational analysis showed that the ground state had $\Omega=4$ which was probably the lowest energy component of an inverted $^3\Phi$ state. This follows the pattern observed for IrF [2, 3], and the isovalent molecules CoH [4] and CoF [5-7], all of which have a $^3\Phi_4$ ground state. Higher resolution LIF spectra with FWHM $\sim 0.006\text{ cm}^{-1}$, taken with a single frequency ring dye laser, showed some line broadening due to unresolved hyperfine structure (hfs) but did not add to or improve the analysis and were therefore not reported.

In order to obtain insight into the electron configurations of the ground and excited electronic states, it is important to be able to resolve the hyperfine structure. This has been previously demonstrated for IrF [3], CoH [8] and CoF [6, 7], where spectra with FWHM $\sim 0.001\text{ cm}^{-1}$, achieved using the laser ablation source and spectrometer at Arizona State University (ASU), showed well resolved hyperfine structure. Analysis of the hfs provided detailed information on the configurational composition of the ground state of each of these molecules and some insight into the excited state configurations. For CoF, further details were obtained from higher resolution microwave spectra [7]. In addition to the hfs analysis, Stark effect experiments studying the behavior of each of the

above molecules in an applied electric field provided more detailed information on the nature of the charge distribution and the bonding mechanism [8, 9].

As expected, the bonding in both CoF and IrF was found to be mainly ionic (M^+F^-) and the ground $X^3\Phi_4$ state of each molecule was found to be a mixture of two configurations [6, 7, 3]:

where $n=3$ for Co and 5 for Ir. For both fluorides, the four open shell configuration was found to be dominant. For CoH the bonding was found to be covalent with the ground $X^3\Phi_4$ state originating primarily from the 2 open shell configuration [4]

with a small contribution from the 4 open shell configuration [6]

In the following sections, we describe experiments performed at ASU to investigate the hyperfine structure and Stark effect in the $[18.0]4 - X^3\Phi_4$ IrH and $[18.2]4 - X^3\Phi_4$ IrD transitions with the aim of examining the bonding and to determine whether the configurational composition of the ground state follows the trend exhibited by CoF, CoH and IrF.

2. Experimental:

The experiments were all performed using the laser ablation spectrometer at ASU. The IrH and IrD molecules were produced by ablating an iridium rod and reacting the resulting Ir atoms with pure hydrogen or deuterium. The equipment and experimental conditions for production, detection and calibration of the Laser Induced Fluorescence

spectra, both field free and in the presence of an electric field, were identical to those previously described in detail for CoF, CoH [8] and IrF [9] and will not be repeated here.

3. Results:

(a) Hyperfine Structure:

The low J transitions of both IrH and IrD showed resolved hyperfine structure which is shown below to be caused almost entirely by the $I = 3/2$ nuclear spin of the ^{191}Ir (37% abundance) and ^{193}Ir (63%) isotopes. It was difficult to distinguish clear patterns in the hydride spectra as there was considerable overlapping of the hyperfine lines. Positive hyperfine assignments could only be made for the Q(4) and P(5) transitions and there were insufficient data for a reliable analysis. The hyperfine structure was much clearer and easier to assign for the deuteride and there was no observed splitting of the lines due to the deuterium hyperfine structure ($I = 1$). The deuteride transitions R(4), R(5), Q(4), Q(5), Q(6), P(5), P(6) were assigned and analyzed. The spectra of the first IrD lines, R(4), Q(4), P(5), are shown in fig. 1. The most intense “main” lines have $\Delta F = \Delta J$ and are labelled with their ground state F values. Weaker “satellite” lines (not labelled) with $\Delta F \neq \Delta J$ can also be seen with significant intensity at low J and are important in breaking the correlation between the upper and lower state hyperfine parameters.

For the least squares fit, the term energies of each state were represented by

$$T = T_{\text{rot}} + W_{\text{mhf}} + W_Q \quad (1)$$

where the rotational energy is given by

$$T_{\text{rot}} = T_0 + B[J(J+1) - \Omega^2] - D[J(J+1) - \Omega^2]^2. \quad (2)$$

The magnetic and quadrupole contributions to the hyperfine energy, W_{mhf} and W_Q , are the diagonal matrix elements of H^{eQq} and H^{mhf} in a Hund's case ($a_{\beta J}$) basis set and are given by [10]

$$W_{\text{mhf}} = h_{\Omega} \Omega \left(\frac{C}{2J(J+1)} \right) \quad (3)$$

and
$$W_Q = eQq_0 \cdot f(J, I, F, \Omega) \quad (4)$$

where
$$f(J, I, F, \Omega) = \frac{[0.75C(C+1) - I(I+1)J(J+1)]}{2I(2I-1)(2J-1)(2J+3)} \left\{ \frac{3\Omega^2}{J(J+1)} - 1 \right\} \quad (5)$$

and
$$C = [F(F+1) - J(J+1) - I(I+1)]. \quad (6)$$

The fits were performed for 46 lines in ^{193}IrD and 42 lines in ^{191}IrD with standard deviations in observed – calculated of 0.0008 and 0.0010 cm^{-1} , respectively. The complete line lists with the assignment, wavenumber and observed – calculated residual for each line are given in the supplementary tables. The results of the fits are listed in Table 1. The upper $[18.2]4$ state was shown in ref. [1] to be perturbed, which is borne out by the anomalous isotope ratio $B(^{193}\text{IrD})/B(^{191}\text{IrD}) > 1$ and the large negative D values. Both the magnetic and quadrupole hyperfine parameters are well determined for both states. The magnitude of both parameters was larger in the upper than the ground state and the quadrupole parameters, eQq_0 , were both negative. Table I also shows that the $^{193}\text{IrD}/^{191}\text{IrD}$ ratio for h_4 and eQq_0 are in reasonable agreement with the ratio of the magnetic and quadrupole moments, respectively.

(b) Stark Effect:

Spectra were obtained for several hyperfine transitions in applied electric fields of $\sim 300 - 1250 \text{ V/cm}$ with the laser polarized parallel and perpendicular to the electric field. The electric field broadened the lines but there were no transitions for which the

individual M_F components were fully resolved and the spectra were not conducive to determining precise dipole moments. However, there was one hyperfine component, $F'=2.5 - F'' = 3.5$, of the P(5) transition of ^{193}IrH , whose linewidth did not increase with the applied field. With the laser polarized parallel to the electric field, there was no noticeable shift or broadening of the line and, with perpendicular polarization, the line split into two lines with no significant broadening. Fig. 2 shows the evolution with increasing electric field of the Stark spectra of the ^{193}IrH P(5) hyperfine components, taken with perpendicular polarization. While the higher frequency hyperfine components are broadened beyond recognition, the $\Delta M_F = +1$ and -1 groups of the $F'=2.5 - F'' = 3.5$ component, each of which consists of six transitions, are clearly seen as narrow lines whose width does not change significantly with the applied field. This indicates that, for this transition, the upper and ground state Stark splittings are the same. This may be used to determine the dipole moments in both states. In the Stark spectrum with perpendicular polarization, the separation of the $\Delta M_F = +1$ and -1 groups will be equal to the separation of the $M_F + 1$ and $M_F - 1$ components in each state. The plot in fig. 3 shows that the separation of the $\Delta M_F = +1$ and -1 groups varies linearly with the electric field. Stark shifts of the energy levels in each state are therefore well represented by the first order diagonal term in the Hamiltonian. The separations of the components at each field are shown in table 2.

The splitting, $\Delta W_{\text{Stark}} = W(M_F+1) - W(M_F)$, of successive Stark levels is given by [11]

$$\Delta W_{\text{Stark}} = \frac{-\mu_{\text{el}} E \Omega [F(F+1) + J(J+1) - I(I+1)]}{2J(J+1)F(F+1)} (0.5034 \text{ MHz/D}) \quad (7)$$

where ΔW_{Stark} is in MHz, μ_{el} is the dipole moment in Debye, and E is the electric field

strength in volts/cm. The spacing of the $\Delta M_F = +1$ and -1 lines in the spectrum is $2\Delta W_{\text{Stark}}$ and is the same for both states when $\Omega = 4$, $J = 4$, $F=2.5$ for the upper state and $\Omega = 4$, $J = 5$, $F=3.5$ for the ground state. Fig. 3 shows a plot of the spacing, $2\Delta W_{\text{Stark}}$ v. E for the $P(5) F' = 2.5 - F'' = 3.5$ transition. The slope of the graph is the same for the upper and lower states of this transition and, by substituting the above values of Ω , J and F for each state into eq. 7, was used to determine the dipole moments of 1.23(1) D and 0.76(1) D for the ground and upper states respectively.

4. Discussion:

4.1 Hyperfine Structure:

The discussion of the hyperfine structure will concentrate on the IrD results as there were insufficient hydride data for a reliable analysis. As there is little or no evidence in the spectra of splitting due to hydrogen or deuterium hyperfine interaction, the hyperfine constants in both molecules can be regarded as resulting entirely from the Ir nuclear spin and would be expected to be the same for the ground state of both molecules. This would not necessarily be true for the upper states as the IrH and IrD transitions involve two different upper states.

(a) Magnetic:

The magnetic hyperfine structure is governed by the effective parameter h_Ω (eq. 3) which is a combination of the Frosch and Foley hyperfine parameters a , b_F and c [12]

$$h_\Omega = a\Lambda + (b_F + \frac{2}{3}c)\Sigma. \quad (8)$$

For $^3\Phi_4$ states, $\Lambda = 3$ and $\Sigma = 1$ and eq. 8 becomes

$$h_4 = 3a + (b_F + \frac{2}{3}c) \quad (9)$$

where

$$a/\text{Hz} = \left(\frac{\mu_o}{4\pi\hbar} \right) g_e g_N \mu_B \mu_N \frac{1}{\Lambda} \langle \Lambda | \sum_i \frac{l_{zi}}{r_i^3} | \Lambda \rangle_l, \quad (10)$$

$$b_F/\text{Hz} = \left(\frac{\mu_o}{4\pi\hbar} \right) \left(\frac{8\pi}{3} \right) g_e g_N \mu_B \mu_N \frac{1}{S} \langle \Lambda \Sigma | \sum_i s_{zi} \delta_i(r) | \Lambda \Sigma \rangle_s, \quad (11)$$

$$c/\text{Hz} = \left(\frac{\mu_o}{4\pi\hbar} \right) \frac{3}{2} g_e g_N \mu_B \mu_N \frac{1}{S} \langle \Lambda \Sigma | \sum_i s_{zi} \frac{(3\cos^2\theta_i - 1)}{r_i^3} | \Lambda \Sigma \rangle_s \quad (12)$$

In Eqs. 10 - 12, $\delta_i(r)$ is the Dirac delta function, s_{zi} and l_{zi} are the one-electron spin and orbital angular momentum operators, θ_i and r_i are the polar coordinates of i th unpaired electron, and Λ and Σ are the total electron orbital and spin molecule fixed projection quantum numbers. In eq. 11, b_F is the Fermi contact parameter and applies primarily to $s\sigma$ orbitals where the expectation value of the $\delta_i(r)$ operator is the spin density, $\psi^2(0)$, at the nucleus.

As only a single $\Omega = 4$ spin-orbit component of each electronic state was observed, it was not possible to determine independent values of a , b_F and c directly from the experimental data and only h_4 could be determined. However, these parameters have been well determined for the ground state of CoH [4] and it is possible to obtain approximate values for IrH and IrD by scaling the CoH values. A rough fit to the very limited IrH data showed that the hyperfine parameters are similar to those of IrD. It is therefore assumed that the calculations below apply equally well to IrH and IrD. This technique has previously been applied successfully to the fluorides [3, 7] and oxides [13, 14]. To a rough approximation, we can expect that, assuming that the Ir and Co atoms experience the same environment in IrD (IrH) and CoH, for similar configurations in the two molecules, the ratio of the a and c parameters will be given by

$$\left(\frac{a(\text{Ir})_{\text{IrH}}}{a(\text{Co})_{\text{CoH}}} \right) \approx \left(\frac{c(\text{Ir})_{\text{IrH}}}{c(\text{Co})_{\text{CoH}}} \right) \approx \frac{g_N(\text{Ir}) \cdot \langle r^{-3} \rangle_{(\text{Ir})}}{g_N(\text{Co}) \cdot \langle r^{-3} \rangle_{(\text{Co})}} = 0.150 \text{ for } ^{193}\text{IrD} [13] \quad (13)$$

For CoH, the parameters, $a = 621.01$ MHz, $b_F = -15.9$ MHz, $c = -456.3$ MHz were determined from Laser Magnetic Resonance experiments [4]. Thus, for IrD, we obtain $a \sim 93$ MHz and $c \sim -68$ MHz and, using our experimentally determined value of $h_4 = 0.00795 \text{ cm}^{-1} = 238$ MHz, we find from eq. 9

$$b_F(\text{IrD}) \approx 238 - 3(93 \text{ MHz}) - \frac{2}{3}(-68 \text{ MHz}) \approx 4 \text{ MHz}.$$

The very small Fermi contact parameter suggests that there is very little contribution from an open shell $s\sigma$ orbital to the ground state configuration of IrD. This would indicate that the two open shell configuration, C (with 5d and 6s replacing 3d and 4s orbitals), is the dominant configuration.

Further evidence favoring the two open shell configuration can be seen in table 3 which compares the metal hyperfine parameters of CoF, CoH, IrF and IrD. For cobalt, the magnetic parameter, h_4 , is greater for the hydride than the fluoride whereas, for iridium, the fluoride has the larger magnetic parameter. To a large extent, the difference between the fluoride and hydride (deuteride) is a reflection of the change in the Fermi contact parameter b_F . For CoF, b_F is negative [6, 7] so that the large increase in h_4 from the fluoride to the hydride is primarily a result of a decrease in the magnitude of the negative Fermi contact parameter. For IrF, b_F was found to be small and positive [3] and the small decrease in h_4 from IrF to IrD (and IrH) is due to a decrease in the magnitude of the positive Fermi contact parameter. Thus, for both Co and Ir, the magnitude of the Fermi contact parameter is smaller for the hydride and deuteride than the fluoride, supporting

the conclusion that, for both Co and Ir, the two open shell configuration plays a more important role in the hydrides and deuterides than in the fluorides.

(b) Quadrupole:

The quadrupole parameter, eQq_0 , is given, in terms of atomic parameters, by [15]

$$eQq_0 = -\left(\frac{e^2}{4\pi\epsilon_0}\right)Q\langle\Lambda\Sigma|\sum_i\frac{(3\cos^2\theta_i-1)}{r_i^3}|\Lambda\Sigma\rangle_1 \quad (14)$$

The quadrupole hyperfine parameters for the ground states of CoF, CoH, IrF and IrD are compared in table 3 where it can be seen that eQq_0 for IrD is 3.4 times larger than for CoH. From eq. 13, the ratio should be determined by the ratio of $Q\langle r^{-3}\rangle$ for the two atoms. Using $Q(\text{Ir}) = 0.75$ Barns, $Q(\text{Co}) = 0.41$ Barns [15], $\langle r^{-3}\rangle(\text{Ir}) = 12.19 \text{ a.u.}^{-3}$, $\langle r^{-3}\rangle(\text{Co}) = 6.71 \text{ a.u.}^{-3}$ [16], gives a calculated ratio of 3.3, in good agreement with the observed ratio.

Both IrF and IrD (and IrH) involve the same Ir orbitals and therefore the calculated hyperfine parameters for the single two open-shell wavefunction and the three possible four open-shell wavefunctions should be the same for IrD and IrH as those calculated for IrF and presented in Table III of ref. 3. The table shows that when the hyperfine structure is entirely due to the Ir atom, the two open-shell configuration leads to a $^3\Phi_4$ state with a positive quadrupole parameter, $eQq_0 = +604 \text{ MHz}$ whereas each of the three possible $^3\Phi_4$ states arising from the four open-shell configuration has a negative $eQq_0 = -604 \text{ MHz}$. The fact that the observed eQq_0 of IrD is negative therefore indicates that, even though the ground states of IrH and IrD arise predominantly from the two open-shell configuration, there is still a significant contribution from the four open-shell configuration.

Any attempt to derive more quantitative conclusions from the above data should be taken with caution. The eQq_0 values for IrF in Table III ref. 3 (and similar values for CoF [7]) for the four open-shell configuration were all based on a configuration involving the Ir $5d\sigma 5d\pi 5d\delta 6s\sigma$ orbitals for which the sum of the $\langle 3\cos^2\theta - 1 \rangle$ terms is $+2/7$. The second σ orbital was treated as pure $6s$ whereas in reality it is almost certainly a $6s6p$ hybrid. As the value of $\langle 3\cos^2\theta - 1 \rangle$ is zero for $s\sigma$ and $+4/5$ for $p\sigma$ [17], eQq_0 will be strongly dependent on the degree of hybridization. For example, including a 10% contribution of $6p$ to the σ orbital would increase the magnitude of eQq_0 for the four open-shell configuration by 28%, i.e. from -604 MHz to -772 MHz.

4.2 Stark Effect:

The discussion will concentrate on the hydride as there were no deuteride transitions in which individual Stark components were resolved or whose width did not alter significantly with increasing electric field. The method used to analyze the Stark spectra of IrH was necessitated by the failure to resolve individual M_F components even at the highest fields. Although this naturally reduced their precision, the resulting dipole moments were still precise enough to examine trends. Table 4 compares the dipole moments of the ground $^3\Phi_4$ states of CoF, CoH, IrF and IrH. It can be seen that IrH follows the trend exhibited by the other molecules, i.e. the dipole moment, μ_e , of the hydride is less than half that of the fluoride and the $\sim 2/3$ ratio of the IrH and CoH dipole moments is similar to that of IrF and CoF.

To gain more insight into the nature of the bonding, the dipole moment is divided by the bond length to give the reduced dipole moment, μ_e/r_e , which leads to the effective nuclear charge shown in row 4 of table 4. For both Co and Ir, the net nuclear charge on

the fluoride is about double that on the hydride. The bond in the fluoride is considerably more ionic than in the hydride and the metal-ligand bond is more ionic with Co than with Ir. An indication of the expected ionic nature of the bond is given by the electronegativity difference between the ligand and the metal. This is shown in the last row of the table and can be seen to be completely consistent with the dipole moment results. The zero electronegativity difference and the small 0.16e charge attest to the covalent nature of the Ir – H bond.

4.3 The Excited States:

Table 1 shows that both the magnetic, h_4 , and quadrupole, eQq_0 , hyperfine parameters show large increases in magnitude on excitation to the $[18.2]4$ state of IrD whereas the dipole moment shows a large decrease on excitation to the $[18.0]4$ state of IrH. In the absence of reliable theoretical calculations, one can only speculate on the nature and possible configurations of the excited $\Omega = 4$ states. A large increase in the magnetic hyperfine constant is often associated with an increase in the Fermi contact term, b_F , caused by an increase in $s\sigma$ character. For example, excitation from the ground $^3\Phi_4$ state to another $^3\Phi_4$ state with an extra unpaired $s\sigma$ orbital must involve excitation from a closed σ^2 shell to an unoccupied $s\sigma$ orbital. One possibility is excitation from the $5d\sigma^2$ orbital in the two open-shell configuration to a higher $s\sigma$ orbital, either 6s or 7s. This transition would therefore involve excitation from the two open-shell $d\sigma^2d\pi^3d\delta^3$ to a four open-shell $d\sigma d\pi^3d\delta^3s\sigma$ configuration. As well as increasing the magnetic hyperfine parameter, the excitation would remove the positive contribution of the two open-shell configuration to the quadrupole parameter (see ref. 3 Table III) resulting in a significant increase in the magnitude of the negative eQq_0 . Although the excited states in the hydride

and deuteride are probably different, the fit to the limited IrH data showed similar significant increases in the hyperfine parameters on excitation suggesting that the same upper state configuration could be involved. The addition of the more polarizable $s\sigma$ orbital is also consistent with a decrease in the dipole moment on excitation.

4.4 Comparison with Theory:

The three ab-initio calculations on IrH [18-20] were discussed in our previous paper [1]. None of them predicted a ground $^3\Phi$ state and, once spin-orbit effects had been considered, the only calculation of excited states placed the lowest $\Omega = 4$ state, a spin-orbit mixture of $^3\Phi_4 + ^1\Gamma_4$, at $\sim 12000 \text{ cm}^{-1}$ above the ground state [18]. The calculated dipole moment, $\mu_e = 1.75 \text{ D}$, is $\sim 50\%$ higher than our experimental value. All of the calculations of the low-lying states were based on a two open-shell configuration with no unpaired $s\sigma$ orbital. There was no consideration of mixing with a four open-shell configuration whose $s\sigma$ orbital would reduce the calculated dipole moment.

5. Conclusion:

The work described above represents the first high resolution study of the spectroscopy of IrH and IrD. The 100 fold improvement in resolution over the only previously reported experimental study [1] has allowed us to examine the hyperfine structure and the Stark effect.

The magnetic and quadrupole hyperfine constants were well determined for both states of IrD. The assumptions made in the interpretation of the ground state hyperfine constants and the uncertainties in the atomic hyperfine parameters precluded precise determination of the Frosch and Foley parameters in eqs. 10 – 12. However, the

calculations involving the magnetic hyperfine parameters still indicated that the two open-shell configuration is the dominant configuration in IrD (and IrH) while the quadrupole parameter showed quite clearly that there is a significant contribution from the four open-shell configuration. The ground state dipole moment of IrH confirms that the Ir-H bond is covalent which is consistent with the electronegativity difference. Both the hyperfine parameters and the dipole moment follow the trend shown by CoF, CoH and IrF.

The above discussion on the excited states highlighted one possible mechanism that would produce an increase in the hyperfine constants and a decrease in the dipole moment on excitation. As the excited $\Omega = 4$ states are almost certainly mixtures of several Hund's case (a) states arising from several different configurations, the true picture will be far more complex than that presented above. While one can only speculate on the excited state configurations, the hyperfine structure and dipole moment can play an important role in limiting the number of possibilities.

There remains a serious discrepancy between theory and experiment as there have so far been no calculations that predict a $\Omega = 4$ ($^3\Phi_4$) ground state for IrH and IrD. The calculation in ref. [18] reproduced reasonably well the vibrational frequency and bond length of the lowest $^3\Phi$ state but placed it too high in energy with a dipole moment that was considerably larger than the observed value. There is an obvious need for further high level calculations for both the ground and excited states and it is hoped that the observations of the hyperfine structure and dipole moment have yielded important insights into the electronic structure and will provide an impetus and guidelines for future calculations.

Acknowledgments

The work at Arizona State University was supported by a grant from the Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy (DE-FG02-01ER15153-A003).

AGA was supported by a grant from the Natural Science and Engineering Research Council of Canada.

References:

- [1] A. G. Adam, A. D. Granger, C. Linton, D. W. Tokaryk, Chem. Phys. Lett. 535 (2012) 21-25.
- [2] A. G. Adam, A. D. Granger, L. E. Downie, D. W. Tokaryk, C. Linton, Can. J. Phys. 87 (2009) 557-565.
- [3] C. Linton, X. Zhuang, T. C. Steimle, A. G. Adam, J. Chem. Phys. 135 (2011) 034305
- [4] S. P. Beaton, K. M. Evenson, J. M. Brown, J. Mol. Spectrosc. 164 (1994) 395-415
- [5] A. G. Adam, W. D. Hamilton, J. Mol. Spectrosc. 206 (2001) 139-142.
- [6] T. C. Steimle, T. Ma, A. G. Adam, W. D. Hamilton, A. J. Merer, J. Chem. Phys. 125 (2006) 64302.
- [7] J. J. Harrison, J. M. Brown, M. A. Flory, P. M. Sheridan, S. K. McLamarrah, L. M. Ziurys, J. Chem. Phys. 127 (2007) 194308.
- [8] H. Wang, X. Zhuang, T. C. Steimle, J. Chem. Phys. 131 (2009) 114315
- [9] X. Zhuang, T. C. Steimle, C. Linton J. Chem. Phys. 133 (2010) 164310.
- [10] A. Carrington, P. N. Dyer, D. H. Levy, J. Chem. Phys. 47 (1967) 1756-1763
- [11] C. H. Townes, A. L. Shawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955)

- [12] R. A. Frosch, H. M. Foley, Phys. Rev. 88 (1952) 1337-1349
- [13] A. G. Adam, C. Linton, T. C. Steimle, J. Mol Spectrosc. 295 (2014) 7-14.
- [14] D. J. Clouthier, G. Huang, A. J. Merer, E. J. Friedman Hill, J. Chem. Phys. 99 (1993) 6336-6344.
- [15] J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge University Press, Cambridge, 2003).
- [16] J. R. Morton, K. F. Preston, J. Magn. Reson. 30 (1978) 577-582
- [17] W. Weltner, Jr., *Magnetic Atoms and Molecules*, (Dover Publications, Inc., New York, 1989)
- [18] D. Dai and K. Balasubramanian. New J. Chem. 15 (1991) 721-726.
- [19] C. Wittborn and U. Wahlgren. Chem. Phys. 201 (1995) 357-362.
- [20] M. Casarrubios and L. Seijo. J. Chem. Phys. 110 (1999) 784-796.

Figure Captions:

Fig. 1: Hyperfine structure in the R(4), Q(4) and P(5) transitions in the 0-0 band of the [18.2]4 – $X^3\Phi_4$ transition of IrD. The main hyperfine lines, with $\Delta F = \Delta J$ are labelled with their lower state F value. The weaker lines, which are not labelled, are “satellite” lines with $\Delta F \neq \Delta J$.

Fig. 2: Field free and Stark spectra of the P(5) transition of the 0-0 band of the [18.0]4 - $X^3\Phi_4$ transition of ^{193}IrH . The Stark spectra were taken with the laser polarized perpendicular to the electric field and show the evolution of the splitting of the $\Delta M_F = +1$ and -1 components of the $F' = 2.5 - F'' = 3.5$ line with increasing field strength.

Fig. 3: Plot showing the linear variation of the splitting, $2\Delta W_{\text{Stark}}$, of the $\Delta M_F = +1$ and -1 components of the $P(5) F' = 2.5 - F'' = 3.5$ line of ^{193}IrH with increasing electric field strength, E . The dipole moments were determined from the slope of the line using eq.7.

Table 1. Parameters for the $[18.2]4 - X^3\Phi_4$ 0-0 band of ^{193}IrD and ^{191}IrD

Parameter (cm ⁻¹)	X ³ Φ ₄		[18.2]4	
	¹⁹³ IrD	¹⁹¹ IrD	¹⁹³ IrD	¹⁹¹ IrD
T ₀	0	0	18254.9688(26)	18255.0249(34)
B	3.37521(10)	3.37561(20)	2.49671(10)	2.49627(20)
10 ⁻⁵ D	1.53(21)	1.63(27)	-313.29(21)	-313.61(27)
h ₄	0.00795(30)	0.00737(30)	0.02045(20)	0.01913(40)
eQq ₀	-0.0105(11)	-0.0107(15)	-0.0437(10)	-0.0426(16)
h ₄ (193/191)	1.080(60) {~1.09 ^a }		1.069(23) {~1.09 ^a }	
eQq ₀ (193/191)	0.98(17) {~0.92 ^b }		1.026(45) {~0.92 ^b }	
	Std. Dev = 0.0008 cm ⁻¹ (¹⁹³ IrD), 0.0010 cm ⁻¹ (¹⁹¹ IrD)			

^a Ratio of the magnetic moments $\mu(^{193}\text{Ir})/\mu(^{191}\text{Ir})$

^b Ratio of the electric quadrupole moments $Q(^{193}\text{Ir})/Q(^{191}\text{Ir})$

Table 2. Stark splitting of the $\Delta M_F = +1$ and -1 components of the $[18.0]4 - X^3\Phi_4$ P(5)

F' = 2.5 - F'' = 3.5 transition of ^{193}IrH	
Field (V/cm)	Splitting (MHz)
0	0
305	66
610	136
1220	268

Table 3: Comparative Ground State Hyperfine Constants (cm^{-1})

	CoF	CoH	IrF	IrD
h_4	0.0325	0.0515	0.00882	0.00796
eQq_0	-0.0027	-0.00309	-0.01003	-0.0105

Table 4. Comparative ground state dipole moment data

	CoF	CoH	IrF	IrH
$\mu(\text{D})$	4.51	1.88	2.82	1.23
$R_e(\text{\AA})$	1.7358	1.531	1.897	1.613
$\mu/R_e(\text{D/\AA})$	2.598	1.278	1.487	0.764
Charge	0.54e	0.26e	0.31e	0.16e
ED ^a	2.100	0.320	1.78	0.00

^a Electronegativity difference (Pauling scale)

IrD Hyperfine Structure