# The permanent dipole moment of ScF $\star$

Benoit Simard, Michael Vasseur<sup>1</sup> and Peter A. Hackett

Laser Chemistry Group, Steacie Institute for Molecular Science, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

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The permanent electric dipole moment of ScF in its X  ${}^{1}\Sigma^{+}$  and C  ${}^{1}\Sigma^{+}$  electronic states has been determined in a pulsed molecular beam apparatus by measuring the Stark shifts on the P(1) and R(0) lines of the (0,0) band of the C  ${}^{1}\Sigma^{+}-X {}^{1}\Sigma^{+}$  system. Values of 1.72(2) and 2.60(5) D have been derived for the X  ${}^{1}\Sigma^{+}$  and C  ${}^{1}\Sigma^{+}$  states, respectively. These values are compared with ab initio data and rationalized in terms of the leading electronic configurations giving rise to the states.

### 1. Introduction

The spectroscopy of small transition metal containing molecules and clusters has been the subject of numerous theoretical [1–3] and experimental [4– 6] studies in the past few years. Nevertheless, much effort is still required in order to rationalize their complicated electronic structure in detail. One parameter that is of great importance towards achieving this goal is the permanent dipole moment,  $\mu$ . This parameter is a gauge of the overall electron charge distribution in the molecule, and is of fundamental importance in description of many phenomena. In particular, it provides a direct way to test theoretical models, especially those emerging from ab initio calculations.

A description of the bonding in transition metal systems is, computationally, very challenging due to the involvement of the metal d electrons in the bonding and the proximity of the metal atomic states with  $ns^2(n-1)d^m$  and  $ns^1(n-1)d^{m+1}$  configurations. Among the systems that have been studied so far, group III transition metal halides appear to be the least difficult as only single ionic bonds are present. They are nevertheless quite complex because of the large number of low lying metal atomic states with  $ns^2(n-1)d^1$  and  $ns^1(n-1)d^2$  occupations.

Recently, in collaboration with Steimle et al., we focused upon yttrium monofluoride (YF), a molecule relatively well characterized spectroscopically and theoretically. The values of 1.82(8) and 2.96(4)D were derived for the dipole moments of the X  ${}^{1}\Sigma^{+}$ and the B  $\Pi$  states, respectively, in somewhat poor agreement with ab initio predictions [7]. In a continuing effort to rationalize the electronic structure and bonding in these systems we now focus upon the smallest and simplest possible transition metal halide: scandium monofluoride (ScF). The low lying electronic states of ScF have been described theoretically by Carlson and Moser [8], Scott and Richards [9], and more recently by Harrison [10], and Langhoff et al. [7]. This work aims at verifying the recent predictions.

The electronic spectrum of ScF has been studied in both the gas phase [11,12] and neon matrices at 4 K [13]. From a comparison of their low temperature absorption spectra with the high temperature gas phase spectra of Barrow et al. [11,12], McLeod and Weltner [13] concluded that the ground state is of  ${}^{1}\Sigma^{+}$  symmetry. In the gas phase at 1750 K [12], several singlet-singlet and triplet-triplet transitions are observed, indicating that the singlet-triplet separation is relatively small. This separation is not known experimentally but the theoretical estimates place the a  ${}^{3}\Delta$  state between 2800 and 3400 cm<sup>-1</sup> above the ground X  ${}^{1}\Sigma^{+}$  state [7]. Many of the observed transitions in the visible have been rotation-

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ally analyzed by Barrow et al. [11,12]. The C  ${}^{1}\Sigma^{+}$ -X  ${}^{1}\Sigma^{+}$  system is very prominent in both the gas phase and low temperature matrices. The (0,0) band of this system is very well suited for Stark experiments as it is easily accessible with narrow linewidth dye lasers, is unperturbed and more importantly, provides a way to measure Stark splittings in both states independently. We report here the first experimental determination of the dipole moment of ScF and compare the values with the most recent ab initio calculations.

# 2. Experimental

The experimental procedure has been described in detail in previous publications [14–16]. Briefly, the ScF molecules were produced in a supersonic molecular beam apparatus by laser vaporizing Sc metal (Johnson Matthew, 99.9%) in the presence of a helium carrier gas doped with < 0.5% of SF<sub>6</sub>.

The Stark plates are made of brass and are separated by  $6.35 \pm 0.05$  mm. The lower plate is grounded. The upper plate is connected to 0-10 kV power supply (Fluka, model 410B) which has a specified accuracy of 0.25%. The fluorescence is viewed through a small hole covered with stainless-steel mesh (95%) transmission). The plates have not been calibrated directly but in our previous work on YF [16] our result for  $\mu(B^{1}\Pi)$  was in agreement with that obtained by Shirley, Scurlock and Steimle at Arizona State University whose plates had been calibrated using CaF [17]. The fluorescence from the ScF molecules was excited by the output of a cw ring dye laser (Coherent 699-29) operating in the kiton-red 620 dye region. Experiments have been carried out with plane polarized laser radiation oriented mainly parallel to the electric field but with some perpendicular contamination. The presence of both polarizations is necessary for the present experiment to ensure that the two Stark components are observed simultaneously, hence permitting a direct determination of the  $M_J = 0 - M_J = 1$  splittings. The Stark splittings were determined from the interference pattern of a thermally stabilized 10 cm confocal etalon (fsr = 750MHz) which were recorded simultaneously.

### 3. Results

As indicated in fig. 1, a study of the R(0) line in the presence of dc electric field with radiation of both polarizations will lead to a direct measurement of the  $M_{I}=1-M_{I}=0$  splittings in the upper state while a study of the P(1) will yield the lower state  $M_J = 1$ - $M_1=0$  splitting. Fig. 2 shows the P(1) line when 0 and 13 kV/cm are applied. The lower trace shows the interferometer pattern used for frequency calibration. Stark splittings for the lower state become measurable at 3.5 kV/cm and fully resolved at 6 kV/ cm. Table 1 gives the measured splittings as a function of the applied dc electric field. Fig. 3 shows the  $\mathbf{R}(0)$  line when 0 and 8 kV/cm are applied. Once again, the lower trace is the frequency calibration. Stark splittings for the upper state become measurable at 2.5 kV/cm and fully resolved at 4 kV/cm. Clearly the dipole moment of the C state is larger than that of the ground state. Table 2 gives the measured



STARK EFFECT IN  $\Sigma - \Sigma$  TRANSITION

Fig. 1. Stark effect in the R(0) and P(1) line of a  $\Sigma-\Sigma$  transition.



Fig. 2. Stark effect on the P(1) line of the C  ${}^{1}\Sigma^{+}-X {}^{1}\Sigma$  (0,0) band of ScF. (A) at 0 V/cm, (B) at 13000 V/cm. The lower figure is the interference pattern of a 10 cm confocal etalon (fsr=750 MHz) used for calibration.

splittings at different electric field strengths.

# 4. Analysis

The dipole moments were determined by fitting the calculated to the observed splittings using a nonlinear least-squares procedure in which the only variable was  $\mu$ . The calculated  $M_J = 1 - M_J = 0$  splittings were obtained by using a  $9 \times 9$  Hamiltonian matrix set up in a case (a) basis set [18,19]. This matrix includes the basis functions associated with the J=0, 1, 2 and 3 levels. The results of the fit are given in

Experimental and calculated  $M_J=1-M_J=0$  Stark splittings (MHz) for the J=1 level of the X  ${}^{1}\Sigma^{+}(v=0)$  state of ScF  ${}^{a_1}$ 

Fields (kV/cm)	Splitting (MHz)		Residual
	expt.	calc.	(MHZ)
3.50	99	115	-16
4.00	109	150	-41
4.50	183	189	-6
5.00	207	233	-26
5.50	237	281	-44
6.00	316	334	-18
6.50	395	391	3
7.00	454	453	1
7.50	500	519	-19
8.00	572	589	-17
9.00	700	740	-40
9.50	800	822	-22
10.0	950	908	42
10.5	1000	998	2
11.0	1080	1091	-11
11.5	1213	1187	25
12.0	1286	1288	-2
12.5	1400	1392	8
13.0	1500	1499	1
13.5	1609	1610	<b>-</b> 1
14.0	1732	1723	8
14.5	1855	1840	14
15.0	1961	1961	0
15.5	2083	2084	-1

<sup>a)</sup> Fitted dipole moment = 1.56 D, standard deviation = 0.0035 D, residual mean squares = 21 MHz.

the third column of tables 1 and 2. The fourth column gives the difference between observed and calculated splittings (residual). In all cases the residual is less than 50 MHz or about 1/3 the observed linewidth. The derived dipole moment is 1.71(2) D for the ground X  ${}^{1}\Sigma^{+}$  state and 2.60(5) for the C  ${}^{1}\Sigma^{+}$ state. The numbers in parentheses represent  $2\sigma$  error estimate in units of the last quoted decimal figure. These uncertainties include the statistical error obtained from the fit and the  $\approx 1\%$  uncertainty in the separation of the plates.

# 5. Discussion

The experimental and calculated dipole moment for ScF and the isovalent species YF are compared in table 3. Although  $\mu(X \ \Sigma^+)$  for YF is larger than



Fig. 3. Stark effect on the R(0) line of the C  ${}^{1}\Sigma^{+}$ -X  ${}^{1}\Sigma^{+}$  (0,0) band of ScF. (A) at 0 V/cm, (B) at 8000 V/cm. The lower figure is the interference pattern of a 10 cm confocal etalon (fsr = 750 MHz) used for calibration.

that for ScF, the ratio  $\mu(X^{\dagger}\Sigma^{+})/r_{e}$ , where  $r_{e}$  is the internuclear distance [20], is essentially the same (0.962 for ScF and 0.966 for YF). This indicates that the bonding in the ground electronic state of these two molecules is equivalent.

A detailed description of the 30 lowest electronic states of ScF has been given by Harrison [10]. For all states examined the bonding is very ionic and the simple single configuration SCF picture corresponds to Sc<sup>+</sup>F<sup>-</sup>. If this dipole lies along the internuclear axis then  $\mu$  should be of the order of 9 D. Clearly this representation is a very poor one. The leading elec-

#### Table 2

Experimental and calculated  $M_J = 1 - M_J = 0$  Stark splittings (MHz) for the J = 1 level of the C  ${}^{1}\Sigma^{+} (v=0)$  state of ScF <sup>a)</sup>

Fields (kV/cm)	Splitting (MHz)		Residual
	expt.	calc.	(MILZ)
3.00	217	219	-2
3.50	266	298	- 31
4.00	395	387	8
4.50	480	488	-8
5.00	578	599	-21
5.50	711	721	-10
6.00	860	853	7
6.50	974	994	- 20
7.00	1174	1145	28
7.50	1322	1305	16
8.00	1468	1474	-6

<sup>a)</sup> Fitted dipole moment = 2.60 D, standard deviation = 0.0085 D, residual mean squares = 17 MHz.

Table 3	
Experimental and calculated dipole moments (D) of ScF	and YF

Species	State	Experimental	Calculated
ScF	X <sup>1</sup> Σ <sup>+</sup>	1.72(2)	1.721 <sup>a)</sup>
	C <sup>I</sup> Σ <sup>+</sup>	2.60(5)	-
YF	$X^{-1}\Sigma^+$	1.86(8) <sup>b)</sup>	1.595 °I
	В'П	2.96(4) <sup>b)</sup>	-

<sup>a)</sup> Ref. [7] using the CPF method augmented with an 18-electron correlation treatment.

<sup>c)</sup> Ref. [7] using the CPF method augmented with a 10-electron correlation treatment.

tronic configuration in the ground state of ScF may be written as [11]:

$$X^{1}\Sigma^{+} = ...(8\sigma^{2} - \lambda 9\sigma^{2})3\pi^{4}10\sigma^{2}$$
.

The  $8\sigma$  and  $9\sigma$  molecular orbitals (MO) are essentially the fluorine  $2p\sigma$  and the scandium  $3d\sigma$  orbitals, between which the single ionic bond is formed. If  $\lambda = 1$  the bonding would be purely covalent and this occurs only at very large internuclear distance. At the equilibrium internuclear distance  $\lambda < 0.1$  and the two bonding electrons are localized essentially in the fluorine  $2p\sigma$  orbital. The  $3\pi$  MOs are essentially the non-bonding fluorine  $2p\pi$  orbitals. The  $10\sigma$  MO is a metal-centered hybrid orbital resulting from the linear combination of the scandium 4s and  $3d\sigma$  or-

<sup>&</sup>lt;sup>b)</sup> Ref. [16].

bitals. According to Harrison [10] this hybridization produces a MO with electron density perpendicular to the internuclear axis. The small dipole moment for X  ${}^{1}\Sigma^{+}$  suggests that the 10 $\sigma$  orbital is more polarized away from the F<sup>-</sup> moiety than suggested by Harrison. Nevertheless, it is clear that the small dipole moment for X  ${}^{1}\Sigma^{+}$  results from the polarization of the 10 $\sigma$  orbital; polarization arising in response to the double occupation of the fluorine 2p $\sigma$ orbital.

The most recent ab initio calculations that report dipole moments are those of Langhoff et al. [7]. The calculated dipole moment for the X  $\Sigma^+$  state of ScF using the coupled-pair functional (CPF) method in which correlation effects among all the 18 outer electrons (3s<sup>2</sup>3p<sup>6</sup>4s<sup>2</sup>3d<sup>1</sup> of Sc+2s<sup>2</sup>2p<sup>5</sup> of F) are included is the same as the experimental value. Lower levels of correlation vield smaller dipole moments. For instance, a 10-electron  $(4s^23d^1 \text{ of } Sc + 2s^22p^5 \text{ of } F)$ treatment lowers the dipole moment by 24% ( $\mu$ (10e)/ $\mu$ (18-e)=0.76). Unfortunately, an 18-electron treatment is not available for YF but a 10-electron treatment gives 1.595 D. It is likely that an 18-electron treatment would reproduce the experimental dipole moment for YF of 1.86(8) D. In summary, the CPF method when used in conjunction with an 18electron correlation treatment reproduces the experimental dipole moment and other spectroscopic parameters of the ground state of ScF quite accurately. Whether the method is applicable for all group III halides remains to be seen. Further experimental and theoretical work are needed.

The C  ${}^{1}\Sigma^{+}$  state results from promotion of a nonbonding 10 $\sigma$  electron into the 11 $\sigma$  MO. The latter orbital is a hybrid resulting from the linear combination of the scandium 4s, 4p $\sigma$  and 3d $\sigma$  orbitals. The resulting MO is much less polarized away from the F<sup>-</sup> moiety. In fact, Harrison's calculation produces an 11 $\sigma$  MO which is slightly polarized towards the F<sup>-</sup> moiety. The result is more electron density along the internuclear axis. This is confirmed experimentally by the larger dipole moment of the C  ${}^{1}\Sigma^{+}$  state, but still less than the dipole moment predicted by the point charge model. There is no theoretical prediction for  $\mu$  for the C  ${}^{1}\Sigma^{+}$  state and any other excited states except the lowest lying a  ${}^{3}\Delta$  state. Reliable calculation of  $\mu$  for these states should be much more challenging because of the contribution of many open-shell configurations.

# 6. Conclusions

The dipole moment of ScF, a very ionic molecule, has been determined by laser Stark spectroscopy to be 1.72(2) and 2.60(5) D for the X  ${}^{1}\Sigma^{+}$  and C  ${}^{1}\Sigma^{+}$ states, respectively. The results are in qualitative and quantitative agreement with the theoretical predictions of Langhoff et al. [7] and Harrison [10] for the X<sup> $\perp$ </sup> $\Sigma^+$  state. For YF the agreement is poorer presumably due to the use of a lower level of electron correlation. It is likely that a CPF 18-electron treatment would be satisfactory for the X  $^{1}\Sigma^{+}$  state of YF. The ability of ab initio calculations to accurately describe ScF and YF appears proven, at least for the ground state. It remains to be seen whether this can be extended to the excited states and other group III halides. Further experimental work in this direction is being carried out in our laboratory. We hope that this will stimulate further theoretical work.

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