Observation of molecular hyperfine structure in the extreme ultraviolet: The HF C-X spectrum

Jeffrey N. Philippson,1 Ralph C. Shiell,1,a Elmar Reinhold,2,b and Wim Ubachs2
1Department of Physics and Astronomy, Trent University, Peterborough, Ontario K9J T8S, Canada
2Laser Centre, Vrije Universiteit, De Boelelaan, 1081 HV Amsterdam, The Netherlands

(Received 3 September 2008; accepted 6 October 2008; published online 7 November 2008)

Clearly resolved hyperfine structure has been observed in the extreme ultraviolet (XUV) spectra of the C \(^1\)\(^1\)\(_\Pi\), \(v=0\rightarrow X \ 1\Sigma^+\), \(v=0\) transition of \(^{19}\)F obtained through 1 XUV+1 UV resonance enhanced multiphoton ionization spectroscopy. The hyperfine splitting within the R-branch lines shows significant perturbations, which we attribute to mixing with the rotational levels of the nearby \(v=29\) level of the B \(^1\Sigma^+\) ion-pair state. A deperturbation analysis quantitatively explains the apparent variation of the fluorine magnetic hyperfine parameter \(a_F\), for which a value of 4034(83) MHz was obtained by averaging over the values derived from the \(R(0)\sim R(4)\) lines, after correcting for the effects of the perturbations. © 2008 American Institute of Physics.

[DOI: 10.1063/1.3006400]

I. INTRODUCTION

For many reasons, hydrogen fluoride (HF) is one of the most intensely studied molecules, both experimentally\(^1\)\(^-\)\(^2\) and theoretically.\(^3\)\(^-\)\(^4\) In common with other hydrogen halides, HF provides a model system for studying molecular dissociation dynamics such as spin-orbit branching\(^5\)\(^-\)\(^6\) and ion-pair formation.\(^7\) Additionally, the large electronegativity of fluorine makes HF an interesting system for studying bond polarity,\(^8\) and it is a well known gain medium within high power chemical lasers.\(^9\)

Hyperfine resolved radio frequency spectra of the ground electronic state splitting due to nuclear spin-rotational and nuclear spin-spin interactions were observed using molecular beam magnetic and electric resonance as early as the 1960s.\(^10\)\(^-\)\(^11\) Early analysis of the electronic spectrum of HF, including identification of the C \(^1\)\(^1\)\(_\Pi\) state and interactions between the \(e\)-parity levels with the corresponding levels in the B \(^1\Sigma^+\) state, was undertaken by Douglas and Greening.\(^12\)\(^-\)\(^13\) Hitchcock et al.\(^11\) performed a detailed experimental and theoretical study of the electronic spectrum, determining absolute cross sections for several bands, and provided a useful overview of previous works. Tashiro et al.\(^14\) used 1 XUV+1 UV (here XUV indicates extreme ultraviolet light, with wavelengths below the LiF cutoff) resonance enhanced multiphoton ionization (REMPI) spectroscopy. The linewidth ranged from 10 to 45 GHz permitting the C \(^1\)\(^1\)\(_\Pi\) levels to be observed with rotational resolution.

Due to the large state densities in this highly excited energy region, interstate perturbations are both significant and numerous\(^15\) and are expected to have strong rotational state dependence. Such perturbations can influence observed hyperfine structure by introducing additional hyperfine splitting into those eigenstates that, to first order, would have no splitting, and concomitantly reducing the observed splitting within other states. A quantitative analysis of this mixing can provide additional insight into the extent of the intramolecular interactions present in this highly excited energy region, one that has historically proven to be challenging both to access and understand.

The work presented herein represents a high-resolution extension of the experiment by Tashiro et al.\(^14\) A linewidth of \(\sim 550\) MHz has allowed us to directly observe hyperfine structure in the C-Rydberg state. Hyperfine resolved spectra of atomic Rydberg states have previously been observed in the VUV (Ref. 16) and XUV\(^15\), while hyperfine structure within molecular Rydberg states has been probed through millimeter-wave spectroscopy following initial excitation in the VUV.\(^18\) To our knowledge, the work presented here is the first example of clearly resolved molecular hyperfine structure in Rydberg states observed through purely optical techniques.

II. THEORY

A. Magnetic hyperfine structure

The presence of nonzero nuclear spin in molecules can split spectral lines into numerous hyperfine components, with energy separations typically orders of magnitude smaller than those associated with the fine structure. The leading terms in the hyperfine Hamiltonian of an isolated molecule represent the energy of each nuclear magnetic dipole moment in the magnetic field due to the electrons, and each nuclear electric quadrupole moment in the electric field gradient. A nucleus with total angular momentum quantum number \(I\sim 1/2\) has no electric quadrupole moment,\(^19\) and therefore the \(^{19}\)F molecule, with two nuclei of spin \(I_f=I_H=1/2\), has no such term in its hyperfine Hamiltonian.

The magnetic dipole hyperfine Hamiltonian includes a summation over the angular momenta of all electrons and nuclei. By projecting this operator onto the subspace of
states within a given vibronic level, an effective Hamiltonian is obtained with terms that depend on either the total electronic orbital angular momentum $\mathbf{L}$ or the total electronic spin angular momentum $\mathbf{S}$. Particular details of the electronic spatial and spin distributions of the chemically important electrons in unfilled subshells can then be obtained from the resulting hyperfine parameters, providing a stringent test of high level theoretical calculations.

The ground state electronic configuration of HF is $1\sigma^22\sigma^23\sigma^21\pi^1\pi^4$. The $C$ $1\Sigma^+$ state derives from the $1\sigma^22\sigma^23\sigma^21\pi^44\sigma$ electronic configuration, where the $1\pi$ and $4\sigma$ nonbonding orbitals are almost entirely of the fluorine $2p_{x,y}$ and $3s$ orbitals, respectively. The $C$ $1\Sigma^+$ state and the experimental resolution we observe, and the order in which the nuclear spins are coupled reflects this hierarchy.

The coupling scheme typically used for a molecule with two nonzero nuclear spins is a direct extension of Hund’s case (a). In case (a), $\mathbf{L}$ is strongly coupled to the internuclear axis by electrostatic forces and $\mathbf{S}$ is coupled less strongly by the spin-orbit interaction. The resulting vector $\mathbf{I}$ is then coupled to the molecular rotation to form $\mathbf{J}$, which is subsequently coupled to the nuclear spin $\mathbf{I}$ to form the total angular momentum $\mathbf{F}$. For the case of $^{19}$F,

$$F = J + I_F,$$

$$F = F_1 + I_{1f}. \tag{1}$$

The basis kets under this coupling scheme can be expressed in the form $| \gamma \Lambda \Sigma J F I_{1f} FM F_F \rangle$, where $\gamma$ represents the electronic configuration and all other quantum labels required to uniquely define each state.

The general theoretical treatment of magnetic hyperfine structure in diatomic molecules is due originally to Frosch and Foley, corrected slightly by Dousmanis, and for states of well-defined $\Lambda$ is now commonly partitioned into four terms representing distinct interactions. The effective Hamiltonian for a molecule with a single nuclear spin is given by

$$\hat{H}_{hfs} = \hat{a} \mathbf{I} \cdot \mathbf{L} + b \hat{\mathbf{S}} \mathbf{I} \cdot \mathbf{S} + \sum_i \left\{ \hat{I}_z^i \mathbf{I} \cdot \mathbf{S} + \frac{1}{2} \hat{I}_z^i (e^{2i\phi^i \mathbf{L} \cdot \mathbf{S}} + e^{-2i\phi^i \mathbf{L} \cdot \mathbf{S}}) \right\}, \tag{3}$$

where the carets explicitly denote operators. For a $^{19}$F molecule in the $C$ $1\Pi$ state, the effective magnetic hyperfine Hamiltonian takes the form

$$\hat{H}_{hfs} = \hat{a}_F \mathbf{I} \cdot \mathbf{L} + \hat{a}_I \mathbf{I} \cdot \mathbf{L}. \tag{4}$$

For each nucleus, $\hat{a}$ is given, in SI units, by the expression

$$\hat{a} = 2g_I\mu_N\mu_B\frac{\mu_0}{4\pi} \frac{1}{\Lambda} \sum_i \frac{\hat{I}_z^i}{r_i^3}. \tag{5}$$

Here, $g_I$ is the respective nuclear $g$-factor, $\mu_N$ is the nuclear magneton, $\mu_B$ is the Bohr magneton, $\hat{I}_z^i$ is the projection on the internuclear axis of the orbital angular momentum of the $i$th electron, which is independent of the nucleus about which the orbital angular momentum is considered, and $r_i$ is the magnitude of the position vector from the relevant nucleus to the $i$th electron. The factor of $\hat{I}_z^i/\Lambda$ within Eq. (5) represents the projection operator $\hat{\Phi}_I$ for Hund’s case (a) molecule, which projects the orbital angular momentum $\mathbf{I}$ of the $i$th electron onto the total electronic angular momentum $\mathbf{L}$.

For the $C$ $1\Pi$ state of $^{19}$F, in the absence of configuration mixing, the only electron for which $\hat{I}_z$ is nonzero is the single unpaired $1\pi$ electron and therefore the expression for $\hat{a}$ reduces to

$$\hat{a} = 2g_I\mu_N\mu_B\frac{\mu_0}{4\pi} \frac{1}{r^3}, \tag{6}$$

where $r$ refers to this single electron and the two orbitals within the $1\pi$ subshell are the $2p_{x,y}$ orbitals of atomic fluorine. The diagonal matrix elements of each term in Eq. (4), for a state $\psi$, are proportional to the respective hyperfine parameter for each nucleus, $a = (\langle \psi | \hat{a} | \psi \rangle \psi)$. These hyperfine parameters reflect the strength of the interaction between each nuclear spin and the electronic orbital angular momentum. Because they are proportional to $(\Sigma \hat{I}_z^i/r_i^3)$, they also contain information about the spatial distribution of unpaired electrons within the molecule.

The hyperfine splitting of the ground electronic state ($\approx$300 kHz) (Ref. 11) is negligible compared to both that of the C-state and the experimental resolution we observe, and this was therefore neglected in the following analysis.

### B. $\Lambda$-doubling

The hyperfine parameter $a$ takes the same value for all rotational levels within a given pure vibronic state, however, for a $1\Pi$-state rotational coupling can lead to mixing of the rotational levels of this degenerate electronic state with the corresponding levels of a $\Sigma$-state. All of the levels of a given $\Sigma$-state have the same $e/f$-parity, and each interacts with states of the same $J$ and parity quantum number in the $\Lambda$-doublet, leading to splitting known as $\Lambda$-doubling. For interaction of a $1\Pi$-state with $\Sigma^\pm$ states, this splitting is given by $qJ(J+1)$, where $q$ is a $\Lambda$-doubling parameter, given by

$$q = 4\sum_{v,\Lambda} \left[ \frac{|(1\Pi v \leftrightarrow J B(R) \Gamma_{1/2}(\mathbf{L})^1 \Lambda^\pm v J)|^2}{E_{v'} - E_v} \right], \tag{7}$$

where the sum over $\Lambda$ is taken over the $\Sigma$-states only, $s$ is an integer that is even for $\Sigma^+$-states and odd for $\Sigma^-$-states, and $B(R)$ is the usual rotational constant at internuclear distance $R$. 


If two states are energetically close, as is often the case for Rydberg states, the precise mixing between rotational states depends critically on their separation. In the case of the \( C^1\Pi, v = 0 \) state in HF, the \( \epsilon \)-parity component of the low-\( J \) levels mixes predominantly with the corresponding rotational level in the nearby \( v = 29 \) vibrational level of the \( B^1\Sigma^+ \) state.\(^{14} \) These \( \epsilon \)-parity levels are probed in the \( R \)-branch \( C-X \) lines, while \( Q \)-branch lines probe the \( \pi \)-parity levels that do not interact with the \( B \)-state. Due to this mixing, we write the energy eigenstate labeled with quantum number \( J \) as

\[
| J \rangle = c_1^J | C^1\Pi, v = 0, J \rangle + c_2^J | B^1\Sigma^+, v = 29, J \rangle.
\]

The projection of this eigenstate onto the \( | C^1\Pi, v = 0, J \rangle \) state determines the mixing fraction

\[
\xi_J = | \langle C^1\Pi, v = 0, J | J \rangle |^2 = | c_1^J |^2.
\]

An effect of this mixing is to introduce hyperfine splitting into those eigenstates that, to first order, derive from the \( B^1\Sigma^+ \)-state and therefore are expected to have negligible hyperfine splitting, and also to reduce the splitting of those states consisting primarily of the \( C^1\Pi \)-state. See Sec. IV for the calculation of these mixing coefficients and their effects on the observed hyperfine structure.

**III. EXPERIMENTAL DETAILS**

The setup of the tunable narrowband XUV radiation source, including its application in high-resolution molecular spectroscopy studies, was described previously.\(^{26} \) In short, the output of a continuous-wave ring-dye laser operating near 570 nm is amplified in a three-stage pulsed-dye amplifier (PDA); then frequency-doubled in a KDP nonlinear crystal and subsequently frequency tripled in a pulsed jet of xenon gas. Coherent radiation, tunable in the wavelength range near 95 nm is produced in a forwardly directed beam at sub-nanosecond pulse energies and at a bandwidth of 250–350 MHz, depending on specific alignment and conditions. This beam is perpendicularly crossed with a molecular beam of HF obtained from a pulsed solenoid valve (General Valve Series 9) and skimmed with a 1 mm diameter orifice. Signal is detected by resonant excitation of lines in the \( C-X \) (0,0) band and subsequent ionization by the UV laser beam that spatially and temporally overlaps the XUV beam. The 1 XUV+1 UV photoionization process produces \( HF^+ \) ions that are detected after pulsed field extraction and time-of-flight mass separation on a particle detector.

In contrast to the earlier experiment,\(^{14} \) no absolute frequency measurements were performed in the present work. Relative frequency measurements are performed by comparing the XUV spectrum with the transmission markers of an actively stabilized etalon, for which the visible output of the ring-dye laser at the fundamental wavelength is used. While in absolute measurements the accuracy of the frequency scale is limited by the effects in the PDA system,\(^{26} \) for the present relative measurements, the uncertainty is reduced to a few megahertz as the pressure is considered to be equal over the small frequency intervals of the scans. Hence the uncertainty in the derived hyperfine parameters is primarily due to the statistics of the fitting procedures.

**IV. RESULTS AND ANALYSIS**

**A. Determination of the \( a_F \) hyperfine parameter**

Each hyperfine-resolved rovibronic line was fitted individually to a simulated spectrum comprising the allowed hyperfine transitions, with the splitting of the upper state rotational level calculated using the Hamiltonian in Eq. (4). The laser system has a primarily Lorentzian profile and the simulated spectra were fitted accordingly, with the full width at half maximum linewidth \( \Delta \nu \) treated as a free parameter in the fit. For the coupling case described above, the allowed electric dipole transitions within each line are given by

\[
\Delta F = 0, \pm 1 \quad (F = 0 \rightarrow F' = 0), \quad \Delta F_1 = 0, \pm 1 \quad (F_1 = 0 \rightarrow F'_1 = 0), \quad \Delta M_F = 0, \pm 1.
\]

The upper state energy splittings were obtained using first-order perturbation theory, resulting in values differing by <5 MHz compared with a full diagonalization approach, and this proved to be much less than the uncertainties in the fitted values of \( a_F \).

For each line, the fitted values of \( a_F \) and \( \Delta \nu \) were varied to minimize the sum of the squared errors between the experimental and simulated spectra. As discussed in Sec. II A, the hyperfine splitting due to the hydrogen nuclear spin was not clearly resolved, making it impossible to obtain the value of \( a_H \) from the fits. This splitting is expected to be small and within this experiment will contribute mainly to a broadening of the observed peaks with negligible effect on the derived value of \( a_F \). A value of 107 MHz was used for the unperturbed value of \( a_H \), predicted by theoretical calculations for the \( X^3\Pi \) state of HF.\(^{25} \) Changes in the distributions of the core electrons are expected to decrease as the ionic limit is approached, and therefore the value for the ionic ground state should closely approximate that for the C-Rydberg state. The mixing fraction between the \( C \) and \( B \) states for each \( J \) was obtained from a deperturbation analysis, as described in Sec. IV B, and multiplied by the unperturbed value of \( a_H \) to provide an effective \( a_H \) in order to fit each \( R \)-branch line.

The matrix elements of Eq. (4) that correspond to the hyperfine energies associated with the \( F \) and \( H \) nuclei are labeled \( ME_F \) and \( ME_H \), respectively,

\[
ME_F = \delta_{IJ} ME_{H,F} a_H \Lambda(\gamma) \times \left\{ \begin{array}{ccc} J & F & I_F \\ I_F & J & 1 \end{array} \right\} E_{F}^{\gamma} - \lambda - 1 F_{i} + 1 + J_{e} + 1 F_{i} + 1 \nu \nu \nu F_{i} + 1 F_{i} + 1
\]

\[
ME_H = \delta_{IJ} ME_{H,F} a_H \Lambda(\gamma) \times \left\{ \begin{array}{ccc} J & F \nu \nu \nu F_{i} & I_H \\ I_H & J & 1 \end{array} \right\} E_{H}^{\gamma} - \lambda - 1 F_{i} + 1 F_{i} + 1 F_{i} + 1 F_{i} + 1
\]

\[
\times \left\{ \begin{array}{ccc} J & F \nu \nu \nu F_{i} & I_H \\ I_H & J & 1 \end{array} \right\} E_{H}^{\gamma} - \lambda - 1 F_{i} + 1 F_{i} + 1 F_{i} + 1 F_{i} + 1
\]
Little is known about the photoionization cross sections from Eqs. (10) and (11), with fitted $a_F$ parameters as shown. The heights of the spectra have been rescaled for clarity.

The relative intensity $S$ of each transition within a line, for linearly polarized incident light and the quantization axis parallel with the electric field, is given by

$$S = (2F + 1)(2F' + 1)(2F_1 + 1)(2F_1' + 1) \times \left\{ \begin{array}{c} F' \ F' \ I_{II} \ H \ F_1' \ J' \ I_F \\ F_1 \ F \ 1 \ J \ F_1 \ 1 \end{array} \right\} \times \left| \sum_{M_F=-F}^{F} \sum_{q=-1}^{1} \left( F' \ 1 \ F \right) \left( J' \ 1 \ J \right) \right|^2. \tag{12}$$

![FIG. 1. REMPI spectra of the C-X transition in H19F, with simulated spectra obtained using the matrix elements of the effective Hamiltonian given in Eqs. (10) and (11), with fitted $a_F$ parameters as shown. The heights of the spectra have been rescaled for clarity.](image)

![FIG. 2. The effects of perturbations between the rotational levels of the $B ^1\Sigma^+$, $v=29$ and $C ^1\Pi$, $v=0$ states of HF. The solid lines represent the energies of the unperturbed states, while the arrows show the energy shifts between perturbed ($e$-parity) and unperturbed ($f$-parity) states.](image)
R-branch transitions in the present study. From the selection rules for electric dipole transitions,27 Q-branch transitions occur between states of different e/ f-parity, while P- and R-branch transitions occur between states with the same parity. Consequently, the upper states of Q-branch C-X transitions in HF are the f-parity components of the A-doublets, which do not mix with the B-state. However, the upper states of the R-branch transitions are expected to have a fitted $a_F$ that varies concomitantly with the mixing fraction $\xi_F$. Figure 3 shows how the values of $a_F$ obtained from fitting the R-branch vary with the upper state $J$-value, and also the mixing fraction $\xi_F$.

Averaging over the fitted $a_F$ values from the $R(0) - R(4)$ lines, after dividing each by its respective mixing fraction, resulted in a value for $a_F$ of 4034(83) MHz. This result assumes that to the experimental precision achieved, the $B^{1}2^{+}$, $v = 29$ state is the only vibronic state to mix with the observed $C^{1}2^{1}$, $v = 0$ levels. The fitted value of $a_F$ from the $Q(1)$ line, for which there are no C-B perturbations, was found to be 4344 MHz, with an estimated uncertainty of $\pm 150$ MHz, determined by comparing the simulated profile for different values of $a_F$ with the extrema of the experimental profile envelope. These two values are in reasonable agreement. Any remaining difference may be due to the presence of other heterogeneous perturbations with states such as the $b^{3}2^{1}$ state discussed by Douglas and Greening.12

From Eq. (6), the hyperfine parameter $a_F$ provides an experimental measurement of $\langle r^{-3}\rangle_{1\pi}$ with respect to the fluorine nucleus. It is interesting to compare this value for the C-state of HF with both that of $\langle r^{-3}\rangle_{1\pi}$ in HF+, and also with $\langle r^{-3}\rangle_{2p}$ in F+. The first indicates the degree of Rydberg character of the C-state, while the second indicates how similar the potential experienced by a $1\pi$ electron in the C-state, for which one electron has been removed from this subshell, is to that of the $2p$ orbital in a singly charged fluoride ion.

Two recent theoretical calculations and two experimental measurements of $a_F$ in HF+ have been published and these values, listed in Table II, are indeed similar to that which we observe in the C-state. Kristiansen and Veseth25 used many-body perturbation theory to calculate a complete set of first-order magnetic hyperfine parameters, allowing a comparison of the electronic spatial and spin distributions because $a/(d + (1/3)c) = \langle r^{-3}\rangle_{\text{orb}}/\langle r^{-3}\rangle_{\text{spin}}$. Bruna and Grein28 used density functional methods to calculate a more restricted set of parameters, with the $a$-parameter obtained from $c$ and $d$, assuming that $\langle r^{-3}\rangle_{\text{orb}} = \langle r^{-3}\rangle_{\text{spin}}$. Coe et al.29 used direct laser absorption spectroscopy in fast ion beams to obtain a complete set of experimentally derived magnetic hyperfine constants. Allen et al.30 used far-infrared laser magnetic resonance spectroscopy to obtain the four magnetic hyperfine parameters.

Our derived value of $\langle r^{-3}\rangle_{\text{orb}}$ for the $1\pi$ orbital is also in reasonable agreement with the calculated corresponding value for the $2p$ orbital of F+.31 The value given in Table II is that derived using polarization wave functions that yield hyperfine parameters in better agreement with experiment than alternative choices of configuration interaction wave functions. The hyperfine structure within the $3P$ ground state of F+ was also studied experimentally by Brown et al.32 using laser magnetic resonance spectroscopy. By combining their experimentally derived value for $a_F$ with the calculated values of $\langle r^{-3}\rangle_{\text{spin}}$ and $|\phi(0)|^2$ from Schaefer and Klemm,31 broad agreement can be seen for the value of $\langle r^{-3}\rangle_{\text{orb}}$. This indicates the validity of the assumed electron configuration of the C-state.

In summary, we have presented results from hyperfine-resolved REMPI spectra of the C-X transition in HF, observed through XUV REMPI spectroscopy with a linewidth of 550 MHz. The R-branch transitions show fitted fluorine magnetic hyperfine parameters that vary with $J$. A quantitative analysis of the rotational coupling between the B and C states has yielded mixing fractions and energy shifts, and largely explains the observed variation in the fitted value of $a_F$. The single value of $a_F$ derived from these spectra is compared with that from a Q-branch line, which does not experience this perturbation.

**ACKNOWLEDGMENTS**

This study was supported by the European Community-Integrated Infrastructure Initiative action LASERLAB-
Europe (RII3-CT-2003-506350) and NSERC (Canada). We wish to acknowledge John Brown for useful discussions. J.N.P. acknowledges Queen’s University for financial support.