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Publication Date

1984

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BY LASER MAGNETIC RESONANCE

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January 1984

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-17292
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Measurement of the Rotational Spectrum of HF^+ by Laser Magnetic Resonance

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Abstract

Rotational transitions in the $X^2\Pi$ state of the HF^+ molecular ion were measured by laser magnetic resonance spectroscopy. Hyperfine splittings from both nuclei were resolved. An analysis of the $J = 3/2 \rightarrow 5/2$ transitions in the $\Omega = 3/2$ spin sublevel is presented.

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Submitted to: Molecular Physics

The first high-resolution study of fluoroniumyl (HF^+), the simplest member of the hydrogen halide ion family, was reported in 1975 by Gewurtz, Lew and Flainek,¹ who photographed the $A^2\Sigma^+ - X^2\Pi$ electronic emission bands from 385-483 nm in a low-pressure discharge with resolution sufficient to determine the principal electronic and structural parameters of the two states. However, the relatively large hyperfine interactions due to the fluorine nucleus were not resolved. Halide hyperfine structure, as studied recently by laser magnetic resonance rotational spectroscopy,² has provided detailed information about the electronic structures of HCl^+ ³ and HBr^+ ⁴. In the present work on HF^+ , we continue our study of this isovalent series of molecular ions. This case is of particular significance: with only nine electrons, HF^+ possesses a structure which can be directly compared with rigorous ab initio calculations.^{5,6}

By directly summing the contributions of both bound and continuum wavefunctions from the shallow $A^2\Sigma^+$ state, Hutson and Cooper⁷ have computed Λ -doubling parameters for the $X^2\Pi$ state with an accuracy comparable to that obtained from emission spectroscopy experiments.¹ Unlike the case for iso-electronic OH, continuum wavefunctions make a large contribution to the ground state Λ -doubling in HF^+ ,⁸ and such low-lying unbound levels are difficult to treat by conventional methods. By examining the spectrum of the $X^2\Pi$ state of HF^+ under the very high resolution available with LMR, we can rigorously assess the reliability of this new direct-sum method. Finally, despite the low cosmic abundance of fluorine, one model of the interstellar medium cites HF^+ as a possible interstellar maser;⁹ accurate rest frequencies obtained from these laboratory measurements will permit an astronomical search.

In this article we report the first detection and a preliminary analysis of rotational transitions in HF^+ , with resolution of both F and H hyperfine splitting. Previous papers^{2,3} describe the details of our LMR spectrometer. Briefly, it consists of a 15-inch electromagnet and an optically pumped far-infrared laser. A beam splitter separates the intracavity sample cell from the laser gain region, and can be rotated to select either σ or π polarization of the laser electric field relative to the magnetic field. The vacuum for the sample region is provided by a Roots pump (Leybold-Heraeus WA-250, 4600 l/min) backed by a mechanical pump (Welch 1396F, 2800 l/min). The HF^+ was produced in the sample region by a 10 mA_{rms} A.C. discharge through helium containing a trace of hydrogen fluoride. Powered at 60 Hz by a Variac stepped up with neon sign transformer, the A.C. discharge system is similar to the D.C. discharge used³ to generate HCl^+ , but causes less plasma noise and degrades the electrodes more slowly. Helium (99.999%) was used without further purification. The HF (Matheson commercial grade) was condensed into a teflon trap at -78°C ; volatile impurities were pumped away. This procedure removes the H_2 formed as HF oxidizes the walls of the lecture bottle. The purified HF was added directly from the trap at room temperature. Spectra were optimized with 0.4 Pa (3 mTorr) HF, and from 40 (0.3 Torr) to 267 (2 Torr) Pa He. The optimum signals were obtained with 90 Pa (700 mT) He (1 Pa = 7.6 mTorr).

Predictions of the $X^2\Pi$ rotational transition frequencies, made with the constants of Gewurtz et al.,¹ indicated suitable coincidences with four known far-infrared laser lines. Using the 122.5 μm CH_2F_2 and 124.4 μm CH_2DOH laser lines, we observed 20 LMR resonances due to the $J = 3/2 \rightarrow 5/2$, $\Omega = 3/2$ rotational transition. With the 184.3 μm CH_2F_2 and 186.0 μm CH_3OH laser lines, the $J = 1/2 \rightarrow 3/2$, $\Omega = 1/2$ rotational transition was measured.

Laser frequencies and magnetic field strengths are presented in Table 1.

Chemical and spectroscopic evidence forms the basis for assigning the spectra to HF^+ . The LMR signals all depend in the same way on the amount of HF added to the discharge, and can not be duplicated using HCl instead; the peaks disappear when the HF is shut off or increased above 2 Pa (15 mTorr). Unpurified HF, which is contaminated by H_2 as noted above, produces weak signals. These observations are explained by the thermodynamics of proton transfer to form H_2F^+ :^{10,11}

Rates for these reactions are not available from the literature, but the analogous reactions for HCl^+ are fast.^{12,13} Laser pulling experiments, which measure the sign of $dH/d\nu$, confirm the position of zero-field predictions made from the optical data of Gewurtz *et al.*¹

The 122.5 μm LMR spectrum shown in Figure 1, as well as the 124.4 μm spectrum, exhibit the pattern expected for a doublet Π state split by two inequivalent spin 1/2 nuclei.¹⁴ The magnitude of the Λ -doubling agrees well with that observed in the optical data of Gewurtz *et al.*¹ The fluorine hyperfine splitting is nearly as large as the Λ -doubling; HCl^+ and HBr^+ likewise show large hyperfine splitting.^{3,4} Proton hyperfine structure appears as a small but clearly resolved doubling for HF^+ , much as it does for isoelectronic OH.¹⁵ By comparison, hydrogen hyperfine structure was not observed in the FIR LMR spectra of the heavier hydrogen halide ions, nor in their neutral analogs SH ¹⁶ and SeH .¹⁷

The $\Omega = 1/2$ state of HF^+ is approximately diamagnetic, since the angular momentum coupling is very near Hund's Case (a); hence, a far-infrared laser

frequency must lie very close to a corresponding zero field transition for it to be tuned into resonance by available magnetic field strengths. Fortunately, two close coincidences exist for HF^+ near the $J = 1/2 \rightarrow 3/2$, $\Omega = 1/2$ transition. The $184.3 \mu\text{m}$ CH_2F_2 laser lies within 50 MHz of one component of the Λ -doublet, while the $186.0 \mu\text{m}$ CH_3OH laser is several hundred MHz from the other component.

An analysis of the $\Omega = 3/2$ transitions was carried out with the high precision $^2\Pi$ Zeeman Hamiltonian of Veseth,^{18,19} evaluated in a Case C_α basis set, and appropriate for a molecule with one nuclear spin. This Hamiltonian has been incorporated into a computer program capable of including both zero field and magnetic resonance spectra in a single weighted least squares fit. Because the program currently is limited to one nuclear spin, the hydrogen hyperfine structure was averaged out and only the much larger fluorine hyperfine pattern was included in this preliminary analysis. The results of the eight parameter fit using both LMR data and combination differences from the emission spectrum¹ are presented in Table 2. We have determined the Case(a)fluorine hyperfine constants h ($h = a + \frac{1}{2}(b+c)$) and b , where a , b , and c are the usual Frosch and Foley parameters. Our analysis also refines the values of the other molecular parameters, particularly the Λ -doubling constants p and q . Hutson and Cooper⁷ calculated the values $p = 7630 \text{ MHz}$ and $q = -1210 \text{ MHz}$, in excellent agreement with the results of our determination. (We have converted their values using the relationship $p = p_{\text{HC}}/2 + q_{\text{HC}}$, $q = q_{\text{HC}}$).

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. Equipment was provided by the National Science Foundation (Grant CHE82-07307). CAF thanks the Brazilian government for a CNPq grant. ES acknowledges a fellowship from NATO through the German Academic Exchange Service.

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Table 1

Observed Laser Magnetic Resonance Transitions for $V = 0$ $X^2\Pi$ HF⁺

Parity ^a	M_J''	M_J'	M_I^b	Flux (Gauss)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
122.5 μm CH_2F_2 ($\nu = 2447969.0$ MHz) $\Omega = 3/2$, $J = 3/2 \rightarrow 5/2$					
-	-3/2	-1/2	1/2	10263.0	-4.1
-	-3/2	-1/2	-1/2	11315.9	-0.1
+	-3/2	-1/2	1/2	12112.0	3.6
+	-3/2	-1/2	-1/2	13182.4	0.3
-	-1/2	1/2	1/2	17511.3	14.7
-	-3/2	-3/2	1/2	17047.2	-1.1
124.4 μm CH_2DOH ($\nu = 2409293.0$ MHz) $\Omega = 3/2$, $J = 3/2 \rightarrow 5/2$					
+	3/2	1/2	1/2	11747.0	4.6
+	3/2	1/2	-1/2	12967.0	-10.6
-	3/2	1/2	1/2	13635.5	-5.3
-	3/2	1/2	-1/2	14863.0	8.4
184.3 μm CH_2F_2 ($\nu = 1626602.6$ MHz) $\Omega = 1/2$, $J = 1/2 \rightarrow 3/2$					
-	1/2	3/2	-1/2	1991.2	*
-	1/2	3/2	1/2	14161.6	*
-	-1/2	1/2	-1/2	3931.9	*
-	1/2	1/2	-1/2	3665.8	*
186.0 μm CH_3OH ($\nu = 1611421.9$ MHz) $\Omega = 1/2$, $J = 1/2 \rightarrow 3/2$					
+	-1/2	1/2	-1/2	1711.8	*
+	1/2	1/2	-1/2	1749.7	*

* Data not included in analysis.

^a Parity of lower state.^b All transitions are $\Delta M_I = 0$. M_I here refers to the fluorine nucleus.^c For fitted lines, flux is averaged ~28G proton hyperfine doublet.
Measurement precision is approximately ± 0.5 G.

Table 2

Molecular Parameters for $V = 0 \text{ X}^2\Pi \text{ HF}^+$ (MHz)*

$$B_0 = 513070.(10)$$

$$D_0 = 66.23(27)$$

$$A = -8736727(400)$$

$$A_D = -847(14)$$

$$p = 7741(19)$$

$$q = -1214.9(18)$$

$$h = 3353(12)$$

$$b = 1384(130)$$

Fixed Molecular g-factors

$$g_\ell = 1.00232$$

$$g_r = 0.00052$$

$$g_s = 2.00232$$

* Numbers in parentheses represent one standard deviation.

Figure Caption

Figure 1. A portion of the HF^+ spectrum recorded with the $122.5\ \mu\text{m}$ CH_2F_2 laser. HF^+ was generated in a 60 Hz discharge operating with 500 V and 9 mA (RMS values) in 94 Pa of helium containing a trace of HF. The data was obtained in a single scan with a time constant of 0.1 sec.

HF⁺

$X^2\Pi_{3/2}$

$M_J = -3/2 \rightarrow -1/2$

$J = 3/2 \rightarrow 5/2$

XBL 841-486

Figure 1

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