

Vibrational mode selectivity in hyperfine interactions: Polarization quantum beat spectroscopy of HCF(\tilde{A}^1A'')

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We report on the vibrational mode dependence of the ^{19}F and ^1H hyperfine interaction constants in the \tilde{A}^1A'' state of HCF, determined using polarization quantum beat spectroscopy. The nuclear spin/overall rotation coupling constants display a pronounced energy dependence and mode selectivity which can be traced to variations in both the A rotational constant and nuclear spin/electron orbital coupling constant a . In particular, modes containing C–F stretching excitation display significantly larger ^{19}F spin-rotation constants, which is explained in terms of a decrease in back donation of electron density into the C $2p_\pi$ orbitals. © 2004 American Institute of Physics. [DOI: 10.1063/1.1640994]

I. INTRODUCTION

Carbenes have importance in areas ranging from organic synthesis to the atmosphere.¹ The chemical interest in carbenes stems from their electronic structure, which gives rise to energetically similar singlet and triplet states with very different chemical properties. As the smallest carbene with a singlet ground state, HCF is a prototype for understanding the spectroscopy, photochemistry, and reactivity of singlet carbenes.^{2–15} The $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ system was first observed in absorption by Merer and Travis (MT),² and subsequently by Hirota and co-workers,^{6–10} who examined the (0,0,0) and (0,1,0) bands under high resolution and probed the ^{19}F hyperfine structure using intermodulated fluorescence.^{7–9}

It is well known that magnetic hyperfine interactions are a sensitive probe of the electron density at the nucleus in question, and thus of the molecular electronic structure. The hyperfine structure is most easily resolved via microwave spectroscopy, which is typically limited to low-lying vibrational states, and thus near-equilibrium nuclear geometries. While electronic transitions often sample a wide range of nuclear geometries, resolving the hyperfine structure of excited electronic states is challenging and, consequently, little detailed experimental information is available concerning the dependence of hyperfine interactions on nuclear coordinate(s). In this Communication we report initial studies concerning the vibrational mode dependence of the ^{19}F and ^1H hyperfine structure in the \tilde{A}^1A'' state of HCF, which provides a beautiful example of vibrational mode selectivity.

II. EXPERIMENTAL SECTION

The apparatus and pulsed discharge nozzle has previously been described in detail.¹⁶ Briefly, HCF radicals were generated by a pulsed electrical discharge through a ~2%

mixture of CH_2F_2 (Aldrich, 99.9%) in argon that was premixed in a stainless steel cylinder. The typical backing pressure was ~1 bar. Discharge was initiated by a negative going 1 kV pulse of typically 10 μs duration that passed through a 10 k Ω ballast resistor. The timing of laser, nozzle, and discharge was controlled via a digital delay generator. The laser system consisted of an etalon narrowed dye laser (Lambda-Physik Scanmate 2E) operating on either Rhodamine 6G, Coumarin 307, Coumarin 102, or Coumarin 47 dye, pumped by the third harmonic of an injection seeded Nd:YAG laser (Continuum Powerlite 7010 or NY61). The laser beam was not focused, and typical pulse energies were ~500 μJ in a ~3 mm diam beam. A quartz window was used to direct a portion of the dye laser fundamental into a Fe-Ne or Fe-Ar hollow cathode lamp for absolute wavelength calibration using the optogalvanic effect. The measurements utilized a mutually orthogonal geometry of laser, molecular beam, and detector, where the laser beam crossed the molecular beam at ~20 nozzle diameters downstream. Fluorescence was collected by a two lens $f/2.4$ condenser assembly, and filtered via an appropriate long-pass cutoff filter (Corion) prior to striking a photomultiplier tube detector (Oriel) held at typically –600 V.

The data collection procedure for quantum beat spectra has also been described in detail.¹⁶ Briefly, fluorescence waveforms are collected in parallel and perpendicular laser-detector polarizations, from which the degree of polarization $[(I_{\parallel}(t) - I_{\perp}(t))/(I_{\parallel}(t) + I_{\perp}(t))]$ is determined. Figure 1 displays typical data at zero-field for the ${}^1R_0(0)$ transition of the (0,1,1) band. The quantum beat spectrum, obtained by Fourier transform of the time-dependent degree of polarization, reveals four beats as illustrated in Fig. 2. Assignments were made based on relative intensities and Zeeman measurements. The high resolving power of QBS (typical resolution: 100 kHz) allows resolution of the small ^1H hyperfine interaction, which is reported here for the first time. The ^{19}F and ^1H hyperfine constants (C_{aa}) were obtained by fitting the observed beat frequencies of the ${}^1R_0(0)$ lines to values cal-

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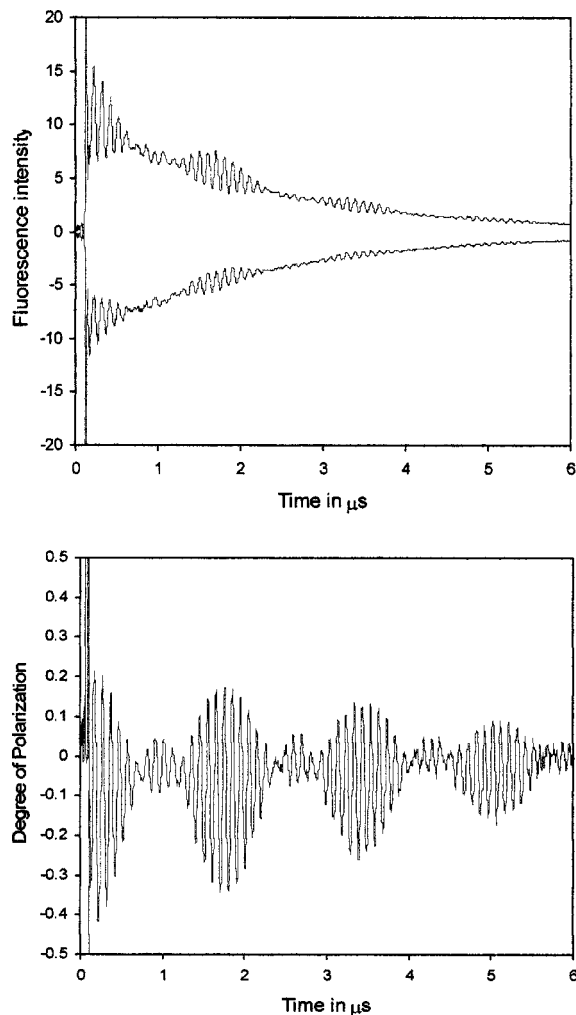


FIG. 1. (Upper panel) fluorescence transients following excitation of the ${}^7R_0(0)$ transition of the (0,1,1) band for parallel (top) and perpendicular orientations of laser and detector polarizations. (Lower panel) time-dependent degree of polarization calculated from the transients in the upper panel.

culated by diagonalizing the 4×4 hyperfine matrix in the case $b_{\beta J}$ basis ($\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_F$; $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_H$).¹⁷ Note that the other diagonal components of the coupling tensor (C_{bb}, C_{cc}) are expected to be at least ~ 25 times smaller and consequently not determinable, and were thus set to zero in the fit.⁹

III. RESULTS AND DISCUSSION

Figure 3 displays the energy dependence of the ${}^{19}\text{F}$ and ${}^1\text{H}$ nuclear spin-rotation constants. Note that the uncertainty is smaller than the symbol size, and our measurement of $C_{aa}({}^{19}\text{F})$ for (0,0,0) of $-8.034(87)$ MHz agrees well with the measurement of Hirota and co-workers [$-7.71(20)$ MHz] using intermodulated fluorescence.⁹ The ${}^{19}\text{F}$ constants increase significantly in magnitude with increasing energy. The ${}^1\text{H}$ constants, while typically much smaller, also appear to increase with energy. We note that the two constants reported for (0,1,0) reflect the two observed $K=1$ subbands, which arise from a perturbation involving a single background \tilde{X}^1A' level. The hyperfine constants for these states are the smallest observed, which is understood by considering that

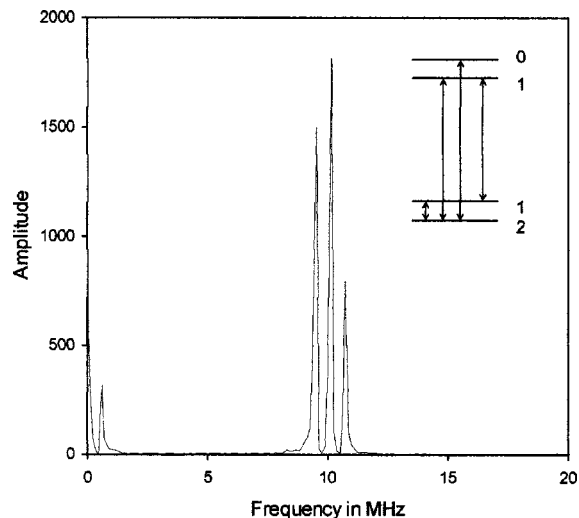


FIG. 2. Quantum beat spectrum of the ${}^7R_0(0)$ transition of the (0,1,1) band, obtained by Fourier transform of the time-dependent degree of polarization shown in the lower panel of Fig. 1. Four beats are clearly observed, and the F state assignments are noted.

the constants for \tilde{A}^1A'' and \tilde{X}^1A' are similar in magnitude but *opposite* in sign. As we will show in a forthcoming analysis of the (0,4,0) band, this partial cancellation of the hyperfine interaction provides a sensitive means of discrimi-

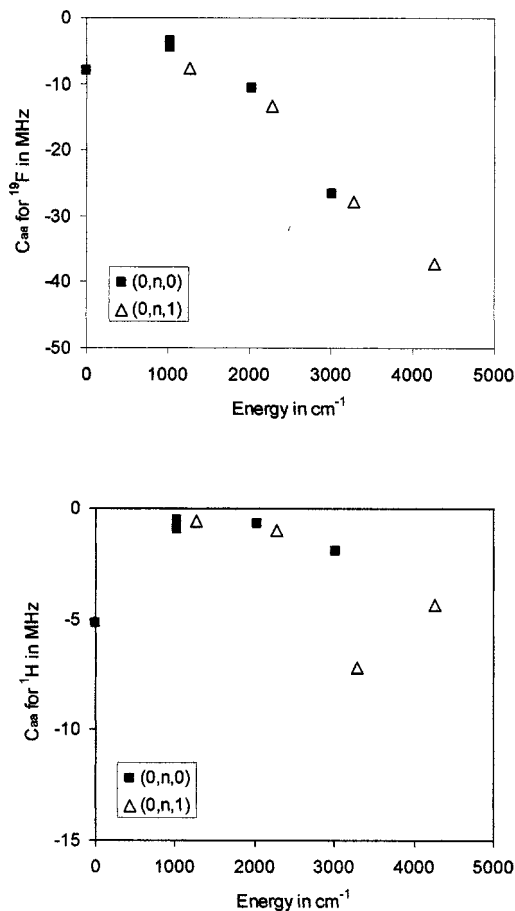


FIG. 3. (Upper panel) hyperfine interaction constants (C_{aa}) for the ${}^{19}\text{F}$ nucleus plotted against vibrational energy. Vibrational state assignments are noted. (Lower panel) similar plot for the ${}^1\text{H}$ hyperfine constants.

nating between perturbations by background singlet and triplet states. We emphasize that none of the other transitions included in the data reported here were identified as perturbed on the basis of spectroscopic analysis and lifetime measurements.¹⁸

Neglecting small terms arising from closed shell electrons and other nuclei, the nuclear spin/overall rotation constant C_{aa} can be written as^{9,19}

$$C_{aa}(v') = -4 \sum_{v''} \frac{\langle \tilde{A}, v' | a L_a | \tilde{X}, v'' \rangle \langle \tilde{X}, v'' | A L_a | \tilde{A}, v' \rangle}{E_{v'} - E_{v''}}, \quad (1)$$

where: A is the a -axis rotational constant, a is the nuclear spin/electron orbital coupling constant, v is a generic vibrational state label, L_a is the orbital angular momentum operator, and the summation runs over all levels coupled to the state in question. We assume here that only \tilde{X}^1A' state levels contribute to this sum.⁹ Using an effective rotational constant A_{eff} , we can rewrite Eq. (1) following the notation of Townes and Schawlow:¹⁹

$$C_{aa}(v') = -4A_{\text{eff}} \sum_{v'} \frac{a_{v'v''} \langle \tilde{A}, v' | L_a | \tilde{X}, v'' \rangle^2}{E_{v'} - E_{v''}}, \quad (2)$$

which indicates that a plot of C_{aa} versus A should be linear. This is indeed the case, at least for the ^{19}F constants, as shown in Fig. 4. The A constants for each band were determined by fitting all unperturbed lines (typically totaling 30–60 in number) in each subband to an asymmetric top Hamiltonian. The lines shown in this figure are linear fits to the ^{19}F data which are meant to guide the eye.

Focusing on the ^{19}F constants in Fig. 4, we observe a clear separation into two groups, with levels containing C–F stretching excitation (0,n,1) falling on one line and the pure bending states (0,n,0) on another. We thus find an obvious increase in the ^{19}F hyperfine interaction for levels containing C–F stretching excitation. For example, $C_{aa}(^{19}\text{F})$ increases by a factor of ~ 1.4 when comparing (0,3,1) to (0,3,0) and a factor of ~ 2.6 for (0,2,1) versus (0,2,0). From Eqs. (1) and (2), we see that this trend must arise from changes in: (1) the a constant, and/or (2) the summation over coupled levels: $\sum_{v''} \langle \tilde{A}, v' | L_a | \tilde{X}, v'' \rangle^2 / (E_{v'} - E_{v''})$. In the absence of any near resonances we expect the latter to be similar for levels containing equal quanta of bend, as the dominant terms in the sum will involve ground state bending levels. Therefore, we tentatively ascribe this trend to the vibrational state dependence of the a constant.

The relatively small ^{19}F hyperfine interaction in HCF arises from loss of electron density via back donation into the carbon $2p_\pi$ orbitals as a result of the strong polarization of the C–F σ bond.⁹ This picture explains the much smaller constant observed for HSiF [$C_{aa}(^{19}\text{F}) < 0.5$ MHz],⁹ as the more strongly polarized Si–F bond increases the level of back donation. It is therefore reasonable that excitation of the C–F stretch, with concomitant elongation of the C–F bond, hinders back donation and increases the magnitude of a . For a more quantitative analysis, it is desirable to determine the nuclear spin/electron orbital (a) constants directly, which will

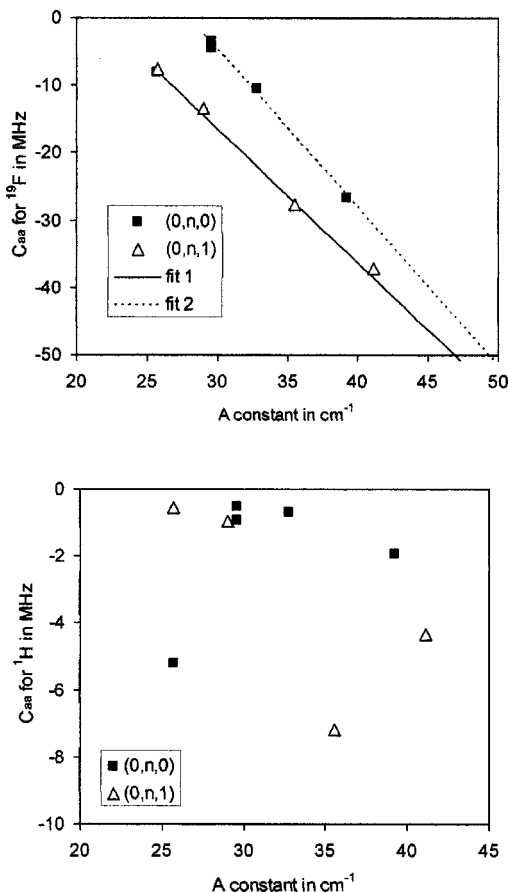


FIG. 4. (Upper panel) hyperfine interaction constants (C_{aa}) for the ^{19}F nucleus plotted against the experimentally determined A constants for the measured vibrational states. To guide the eye, linear fits to the data are also shown. (Lower panel) similar plot for the ^1H hyperfine constants.

be possible by combining these results with Zeeman measurements. Such measurements are now underway and will be reported in a future publication.

There exist in the literature very few studies of the vibrational mode dependence of hyperfine interactions for polyatomic molecules, and none we are aware of for excited electronic states apart from recent work on NO_2 ,^{20–22} where strong vibronic coupling precludes detailed vibrational state assignments, and HCP,²³ where vibrational state assignments are also uncertain. Of course, more data is available for ground electronic states, particularly for NO_2 ,^{24–26} NH_3 and related C_{3v} molecules,^{27–30} and a few others.^{31–38} The data set for NO_2 is perhaps the most extensive, and shows no systematic change in the hyperfine parameters for different vibrational modes.²⁵ In contrast, some variation in quadrupole coupling constant(s) with vibrational mode has been observed for several molecules.^{27,31,32,38} This has been an active area for theorists,^{39–42} and we plan in the future to compare our results with high level *ab initio* calculations.

In summary, we have reported our initial results concerning the vibrational mode dependence of the ^{19}F and ^1H hyperfine interaction in $\text{HCF}(\tilde{A}^1A'')$. The ^{19}F nuclear spin/overall rotation coupling constants display a pronounced energy and mode selectivity which is reasonably explained in terms of variations in both the rotational constant A and

nuclear spin/electron orbital coupling constant a . In particular, excitation of modes containing C–F stretching quanta is found to increase the ^{19}F spin-rotation interaction, which is explained in terms of a decrease in back donation to the $C2p_\pi$ orbitals. It is anticipated that Zeeman measurements in combination with these results will provide a detailed glimpse into the electronic structure of this prototypical carbene.

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