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Lifetime lengthening and the Renner–Teller effect in the HCF ($\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$) system

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8 Abstract

9 We report new measurements of fluorescence excitation spectra and single rovibronic level fluorescence lifetimes for
10 $(0, v_2', 0) \leftarrow (0, 0, 0)$ bands with $v_2' = 0-6$ in the HCF $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ system. Due primarily to the Renner–Teller in-
11 teraction, upper state levels with $K_a \geq 1$ display an obvious lengthening of lifetime with increasing energy which is
12 strongly correlated with the presence of vibronic and rovibronic perturbations, and increases dramatically as the barrier
13 to linearity is approached. This system provides a textbook example of the small molecule limit of radiationless
14 transitions.

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17 1. Introduction

18 Carbenes have importance in areas ranging
19 from organic synthesis to the atmosphere [1]. As
20 the smallest carbene with a singlet ground state,
21 HCF is a prototype for understanding the spec-
22 troscopy, photochemistry, and reactivity of singlet
23 carbenes [2–15]. The $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ system was
24 first observed in absorption by Merer and Travis
25 (MT) [2], who reported a progression in the
26 bending vibration. Rotational analysis was per-
27 formed for the $(010) \leftarrow (000)$ and $(000) \leftarrow (000)$
28 bands, revealing a bent structure in both states.
29 The large change in bond angle (opening by $\sim 25^\circ$

in the excited state) led to prominent axis-switching 30
ing transitions, in addition to those obeying the 31
normal selection rules for a perpendicular transi- 32
tion. Subsequently, Hirota and co-workers [6–10] 33
reexamined these bands under high resolution, and 34
reported Zeeman studies which showed that the 35
magnetic properties of \tilde{A}^1A'' arise primarily from 36
interactions with high vibrational levels of \tilde{X}^1A' . 37
In addition, some local triplet state perturbations 38
were identified [7–9]. 39

Previously, radiative lifetimes for the levels 40
 $(0, v_2', 0)$, $v_2' = 0-3$, were measured at room tem- 41
perature by Ashfold et al. [5], who reported a life- 42
time of 2.45(10) μ s for (0,0,0) which decreased to 43
1.85(10) μ s for (0,3,0). Subsequently, Ibuki et al. 44
[13] observed HCF emission following the VUV 45
photodecomposition of CHFBr₂, and determined a 46
lifetime of 2.57(16) μ s. Recently, Schmidt et al. [15] 47

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48 reported a lifetime of ~ 250 ns for (0,6,0), signifi- 93
49 cantly shorter than expected from extrapolation of 94
50 the lower energy values, which was attributed to a 95
51 decreased fluorescence quantum yield arising from 96
52 fast non-radiative decay to \tilde{X}^1A' . This result is 97
53 unanticipated for such a small molecule, given that 98
54 for CH_2 and CD_2 the Renner-Teller coupling has 99
55 been shown to give rise to *longer* lifetimes for levels 100
56 with $K_a \geq 1$ [16,17]. 101

57 Among the halocarbenes, HCF provides the 102
58 best opportunity to examine the onset of the 103
59 Renner-Teller interaction, as the barrier to line- 104
60 arity is calculated to lie ~ 6800 cm^{-1} above the 105
61 (0,0,0) level [14]. Moreover, the calculated thresh- 106
62 old to dissociation into H and CF lies only slightly 107
63 higher, over a small barrier [14]. To gain further 108
64 insight into the \tilde{A}^1A'' state dynamics for this pro- 109
65 totypical carbene, we conducted detailed mea- 110
66 surements of the energy dependence of the 111
67 fluorescence lifetimes, fluorescence excitation 112
68 spectra, hyperfine structure, and magnetic prop- 113
69 erties. This Letter reports on the former, which is 114
70 shown to provide a textbook example of lifetime 115
71 lengthening. 116

72 2. Experimental

73 The apparatus and pulsed discharge nozzle has 117
74 previously been described in detail [18]. Briefly, 118
75 HCF radicals were generated by a pulsed electrical 119
76 discharge through a $\sim 2\%$ mixture of CH_2F_2 (Al- 120
77 drich, 99.9%) in argon that was premixed in a 121
78 stainless steel cylinder. The typical backing pres- 122
79 sure was ~ 1 bar. Discharge was initiated by a 1 kV 123
80 pulse of typically 10 μs duration that passed 124
81 through a 10 k Ω ballast resistor. The timing of 125
82 laser, nozzle, and discharge firing was controlled 126
83 by a digital delay generator, which also generated 127
84 a variable width gate pulse for the high voltage 128
85 pulser. The laser system consisted of an etalon 129
86 narrowed dye laser (Lambda-Physik Scanmate 2E) 130
87 operating on either Rhodamine 6G, Coumarin 131
88 307, Coumarin 102 or Coumarin 47 dye, pumped 132
89 by the third harmonic of an injection seeded 133
90 Nd:YAG laser (Continuum Powerlite 7010 or 134
91 NY61). The laser beam was not focused, and 135
92 typical pulse energies were ~ 500 μJ in a ~ 3 mm 136

diameter beam. A quartz window was used to di- 93
rect a portion of the dye laser fundamental into an 94
Fe-Ne or Fe-Ar hollow cathode lamp for absolute 95
wavelength calibration using the optogalvanic ef- 96
fect. 97

Spectroscopic measurements utilized a mutually 98
orthogonal geometry of laser, molecular beam, 99
and detector, where the laser beam crossed the 100
molecular beam at a distance of ~ 10 mm down- 101
stream. For lifetime measurements, the beam 102
source was oriented on the detector axis to mini- 103
mize the effects of flyout. Fluorescence was col- 104
lected by a two lens $f/2.4$ condenser assembly, and 105
filtered via an appropriate long-pass cutoff filter 106
(Corion) prior to striking a photomultiplier tube 107
detector (Oriel) held at typically -600 V. For 108
spectral acquisition, the PMT signal was termi- 109
nated into 15 k Ω and digitized by a fast oscillo- 110
scope (HP 54521A), and a 'fast scan' mode was 111
employed, where ten laser shots were averaged in 112
the baseline and 30 laser shots on the peaks. For 113
lifetime measurements, the signal was terminated 114
into 50 Ω and digitized at a typical sampling rate 115
of 250 MHz. Waveforms were averaged typically 116
over 2000 laser shots, with five decays individually 117
fit and the results averaged for each transition. 118

119 3. Results and discussion

Fig. 1 displays the results of our lifetime mea- 120
surements, sorted as a function of K'_a . Note that 121
the uncertainties are smaller than the symbol size. 122
Considering the (0,0,0) level, which for the range 123
of J and K_a studied here is essentially unperturbed 124
[2,6], we find little dependence of the lifetime on J 125
or K_a , and the average lifetime of ~ 2.38 μs is very 126
consistent with the room temperature measure- 127
ment [5]. All levels with $v'_2 > 0$, however, show 128
some variation in lifetime with K'_a . Comparing 129
lifetimes for $K'_a = 0$ with those for $K'_a \geq 1$, the 130
former decrease nearly monotonically with in- 131
creasing v'_2 , as expected from the cubic wavelength 132
dependence. However, those for $K'_a = 1$ and 2 ex- 133
hibit striking non-monotonic behavior, and above 134
(0,3,0) *increase* dramatically with increasing v'_2 . 135
With the increase comes also significant fluctua- 136
tion from level to level within a given sub-band. 137

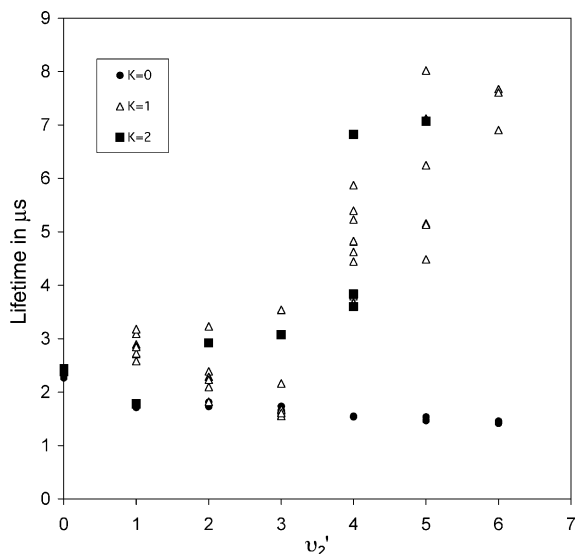


Fig. 1. Energy dependence of the fluorescence lifetimes for single rovibronic levels in the $K'_a = 0, 1,$ and 2 sub-bands of the pure bending states $(0, v'_2, 0)$ with $v'_2 = 0-6$.

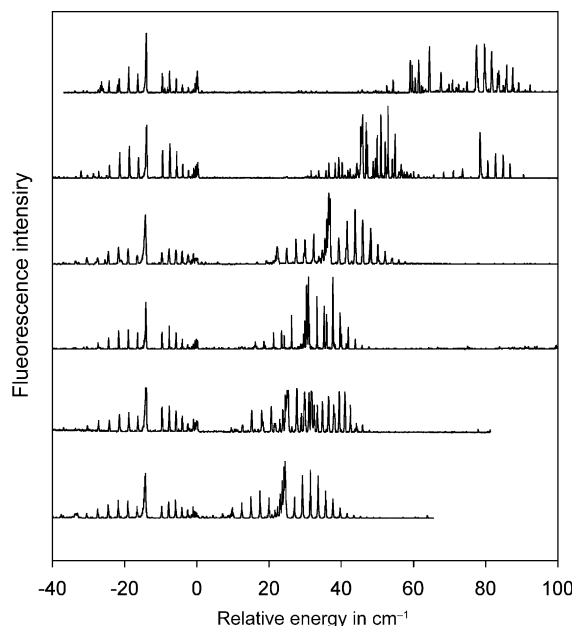


Fig. 2. Fluorescence excitation spectra of the pure bending states $(0, v'_2, 0)$ with $v'_2 = 0-5$ in the region of the $K'_a = 0 \leftarrow K''_a = 1,$ $K'_a = 0 \leftarrow K''_a = 0,$ and $K'_a = 1 \leftarrow K''_a = 0$ sub-bands. The $(0,0,0)$ spectrum is at bottom, and that of $(0,5,0)$ at top. In each spectrum the position of the forbidden $K'_a = 0 \leftarrow K''_a = 0$ sub-band has been set at 0 cm^{-1} , and the intensities were scaled for ease of comparison.

138 For example, in $(0,4,0)$ the $K'_a = 0$ lifetimes vary by
139 less than 1%, while those for $K'_a = 1, 2$ vary by
140 almost 100%!

141 The lengthening of lifetime for $K'_a \geq 1$ is oppo-
142 site the trend suggested by Schmidt et al. [15] on
143 the basis of their $(0,6,0)$ measurement, and indi-
144 cates a dilution and/or weakening of the transition
145 moment. Dilution is obviously occurring, based on
146 the rovibronic perturbations observed in sub-
147 bands with $K'_a \geq 1$. To illustrate, Fig. 2 displays
148 fluorescence excitation spectra in the region of the
149 $K'_a = 0 \leftarrow K''_a = 1,$ $K'_a = 0 \leftarrow K''_a = 0,$ and $K'_a =$
150 $1 \leftarrow K''_a = 0$ sub-bands of the $(0, v'_2, 0) \leftarrow (0, 0, 0)$
151 bands with $v'_2 = 0-5$. The sub-bands terminating in
152 $K'_a = 0$ are unperturbed, while perturbations in the
153 $K'_a = 1 \leftarrow K''_a = 0$ sub-band exhibit a striking en-
154 ergy dependence. For $(0,1,0)$ the perturbation in-
155 volves a single background \tilde{X}^1A'' level [8], and all
156 states display a lengthened lifetime with relatively
157 small scatter for different J states (Fig. 1). In
158 $(0,2,0)$ and $(0,3,0)$ only scattered rotational per-
159 turbations are observed, and longer lifetimes are
160 observed for these states, with unperturbed states
161 displaying a lifetime similar to that of $K'_a = 0$. In
162 contrast, for $(0,4,0)$ and $(0,5,0)$ this sub-band is
163 extensively perturbed, and the lifetimes are much

164 longer on average with significant state-to-state
165 fluctuations. We emphasize that in this case the
166 clump of eigenstates resulting from a single bright
167 state can typically be identified using combination
168 differences, and the clean excitation of single ei-
169 genstates is typically possible.

170 The drastic lengthening in lifetime for levels
171 with $K'_a \geq 1$ correlates with the onset of the barrier
172 to linearity, as viewed in the increase in rotational
173 constant A for the pure bending states (Fig. 3).
174 Note that our values are consistently larger than
175 those of Schmidt et al. [15], who estimated A from
176 the separation of the 1Q_0 and 3Q_0 bandheads,
177 while we conducted global fits to all unperturbed
178 levels in each sub-band. Although we have ob-
179 served isolated triplet state perturbations, the
180 trends in lifetime implicate the Renner-Teller in-
181 teraction [16,17], which scales with A and reaches a
182 maximum in the barrier region. As additional evi-
183 dence, in Fig. 4 is compared the ratio of integrated

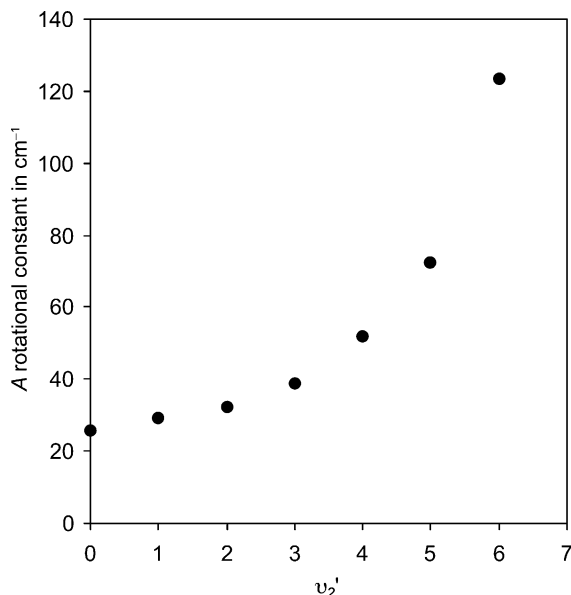


Fig. 3. Derived A rotational constants for the pure bending states $(0, v_2', 0)$ with $v_2' = 0-6$.

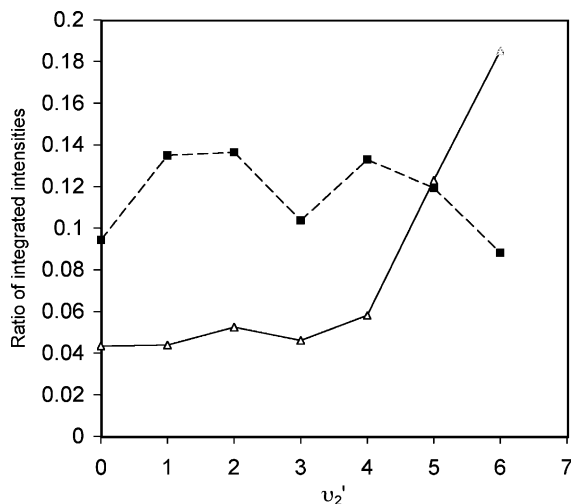


Fig. 4. Ratio of integrated intensities of the forbidden $K_a' = 0 \leftarrow K_a'' = 0$ sub-band to that of the $K_a' = 0 \leftarrow K_a'' = 1$ sub-band (closed symbol/dashed line) and the $K_a' = 1 \leftarrow K_a'' = 0$ sub-band (open symbol/full line) for the pure bending states $(0, v_2', 0)$ with $v_2' = 0-6$.

184 intensities of the forbidden $K_a' = 0 \leftarrow K_a'' = 0$ sub-
185 band to that of: (a) the $K_a' = 0 \leftarrow K_a'' = 1$ sub-
186 and (b) the $K_a' = 1 \leftarrow K_a'' = 0$ sub-band. Of course,
187 the former will depend on rotational temperature,

but this was quite constant across our measurements. The ratio of integrated intensities for the bands terminating in $K_a' = 0$ remains relatively constant, while that for $K_a' = 0$ vs. 1 is also approximately constant up to $v_2' = 4$ but increases as the barrier to linearity is approached, reflecting the onset of strong perturbations. It is worth noting that in HCCl, where the barrier to linearity is much lower, only sub-bands terminating in $K_a' = 0$ appear strongly in the spectrum, and transitions to levels with $K_a' = 1, 2$ are always very weak and strongly perturbed [19].

Lifetime lengthening is a hallmark of the small molecule limit of radiationless transitions [20,21]. Of course, this effect was first observed by Douglas [21] in the spectra of NO₂ and SO₂. Other beautiful examples include the studies of ter Horst and Kommandeur [22] on *para*-benzoquinone, Qian et al. [23] on NCNO, Dunlop and Clouthier [24] on thioformaldehyde, and the afore-mentioned studies of methylene [16,17]. However, rarely in these studies were single eigenstates resolved, and often a quantitative comparison was hampered by uncertainties in the radiative lifetime. In our case the unperturbed $K_a' = 0$ levels provide a convenient baseline for quantitative comparison (Fig. 1), and other factors conspire to make the $\hat{A}^1A'' \leftarrow \hat{X}^1A'$ system of HCF a textbook example of lifetime lengthening. The background level density is relatively small and the coupling matrix elements are relatively large, e.g., ~ 0.4 cm⁻¹ on average for $(0,4,0)$, which allows the clean excitation of single-molecular eigenstates. Unlike the case of HCO [25], where the opposite trend is observed, the ground state is stable with respect to dissociation at these energies.

4. Summary and conclusions

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We have reported new results involving fluorescence excitation spectroscopy and single rovibronic level lifetime measurements of the $(0, v_2', 0) \leftarrow (0, 0, 0)$ bands with $v_2' = 0-6$ in the HCF $\hat{A}^1A'' \leftarrow \hat{X}^1A'$ system. Due primarily to the Renner-Teller interaction, upper state levels with $K_a \geq 1$ display an obvious lengthening of lifetime with increasing energy which is strongly correlated

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233 with the presence of vibronic and rovibronic per-
234 turbations, and increases dramatically as the bar-
235 rier to linearity is approached. Future work will
236 seek to probe higher bending levels, above the
237 barriers to linearity and reaction, and calculate
238 vibronic transition moments in the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$
239 system [16]. Finally, we note that the full results
240 of our spectroscopic studies will be published
241 elsewhere.

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