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Fluorescence Excitation and Emission Spectroscopy of the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ System of CHI and CDI[†]

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We report on the first detailed studies of the spectroscopy of an iodocarbene, measuring fluorescence excitation and emission spectra of the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ system of :CHI and the deuterated isotopomer :CDI. Due to similar bending and C−I stretching frequencies in the upper state, fluorescence excitation spectra of :CHI show polyads composed of members of the $2_0^{n-x}3_0^x$ progressions with $x = 0-3$. For :CDI, only progressions with $x = 0, 1$ are observed. Extrapolation of the 2_0^n term energies for both isotopomers to a common origin places the electronic origin of the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ system near 10 500 cm^{-1}, in good agreement with theoretical predictions. Rotational analysis of the 16 observed bands for CHI and 13 observed bands for :CDI yields rotational constants for the upper and lower states that are also in good agreement with theory. To investigate the controversial issue of the ground state multiplicity of :CHI, we measured single vibronic level emission spectra from many $\tilde{A}^1A''$ levels. These spectra show conclusively that the ground state is a singlet, as for both isotopomers the $\tilde{a}^3A''$ origin is observed, lying well above the origin of the $\tilde{X}^1A'$ state. At energies above the $\tilde{a}^3A''$ origin, the spin−orbit mixing is so severe that few vibrational assignments can be made. Analysis of the emission spectra provides a lower limit on the singlet−triplet gap of 4.1 kcal mol^{-1}, in excellent agreement with theoretical predictions.

Introduction

Carbenes are an important class of reactive intermediates that characteristically contain a divalent carbon atom, and the reactivity of singlet and triplet carbenes has been extensively studied over the past 50 years.[1] As the smallest carbenes with singlet ground states, the monohalocarbenes (:CXY; X = H, F, Cl, Br, I; Y = F, Cl, Br, I) have served as important prototypes for understanding the spectroscopy of carbenes, and benchmarks for theoretical predictions of carbene singlet−triplet gaps. Over the past three decades many theoretical studies have appeared on the topic, using a variety of ab initio methods.[2−44] Experimental studies of the singlet−triplet gap, while less numerous, have also exploited a variety of techniques, including negative ion photoelectron spectroscopy (PES),[45−47] emission spectroscopy,[48−66] and stimulated emission pumping (SEP) spectroscopy.[67−70] The SEP method was first demonstrated in the laboratory of Robert W. Field in the late 1970s,[71−73] and it is a pleasure for us to contribute to this volume in his honor.

Lineberger and co-workers developed the negative ion PES method to examine carbene singlet−triplet gaps,[45−47] and in 1992 reported polarization-specific PES spectra of the monohalocarbene anions.[46] For :CHF, the determined ΔE_{ST} of 14.9(4) kcal mol^{-1} is in excellent agreement with theory. Derived ΔE_{ST} values (in kcal mol^{-1}) for the heavier monohalocarbenes were 4.2(25) for :CHCl, 2.6(22) for :CHBr, and −4 to −10 for :CHI (note that a negative value indicates a triplet ground state). At the time, no theoretical predictions were available concerning ΔE_{ST} for :CHI; however, several theoretical papers on the subject promptly appeared.[20,22,23,28,32] All of these gave ΔE_{ST} values around 4 kcal mol^{-1}, revealing a significant discrepancy between experiment and theory.

Over the past decade, several experimental groups, including our own, initiated detailed spectroscopic studies of the monohalocarbenes.[48− 55,58−66,68−70,74−101] Despite this large body of work, only last year was the spectrum of an iodocarbene, :CHI, reported by us after an extensive effort.[66] The vibronic assignments in the electronic spectrum were unclear, as only bands lying quite far above the origin were measured, yet this work established a singlet multiplicity for the ground state and gave a lower limit on the singlet−triplet gap of 3.76 kcal mol^{-1}, using a deperturbation analysis of SVL emission spectra. In this work, we report the full results of our :CHI experiments, and the first measurement of excitation and emission spectra of the deuterated isotopomer, :CDI. Our experimental results are compared with a variety of ab initio calculations.

Experimental Section

The apparatus, pulsed discharge nozzle, and data acquisition procedures have been described in detail in earlier studies.[48−55,65,66,68−70,81−90] Briefly, :CHI (:CDI) was typically generated by a pulsed electrical discharge through a mixture of CH_3I (CD_3I) in He, obtained by passing high purity He gas through a stainless steel bubbler containing the chemical. The bubbler was placed in a refrigerated bath that was typically held at −10 °C, and the backing pressure was ~2 bar. In early experiments, a room temperature mixture of CH_2I_2 (CD_2I_2) and CHI_3 (CDI_3) was used; however, we found that CH_3I (CD_3I) gave the largest :CHI (:CDI) signals. The discharge was initiated by a +1000 V pulse of 50 μs duration, through a current limiting 10 kΩ ballast resistor. The timing of laser, nozzle, and discharge firing was controlled by an eight channel digital delay generator (Berkeley Nucleonics model 565), which also generated a variable width gate pulse for the high voltage pulser (Directed Energy GRX-1.5K-E). The laser system was an tunable dye laser (Sirah Cobra Stretch) pumped by the second harmonic of

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a Nd:YAG laser (Spectra Physics INDI). The laser beam was not focused, and typical pulse energies were ~1−2 mJ in a ~3 mm diameter beam. A portion of the dye laser fundamental was sent into a Fe−Ne or Fe−Ar lamp for absolute wavelength calibration using the optogalvanic effect.

These measurements utilized a mutually orthogonal geometry of laser, molecular beam, and detector, where the laser beam crossed the molecular beam at a distance of ~15 mm (19 nozzle diameters) downstream. Fluorescence was collected and collimated by a *f*/2.4 plano-convex lens, and focused using a second 2 in diameter *f*/3.0 lens either (a) through a long-pass cutoff filter onto a photomultiplier tube detector (PMT, Oriel 77348) for monitoring total fluorescence or (b) onto the slit of a 0.3 m spectrograph (ANDOR Schamrock) equipped with a gated intensified charge coupled device detector (ICCD; ANDOR Istar) for wavelength resolved emission spectra. A slit width of 250 μm was typically used, and background spectra were obtained with the laser blocked to identify emission lines from the discharge. The spectrograph was calibrated using emission lines from a Fe:Ne hollow cathode lamp.

Fluorescence excitation spectra were acquired by integrating the PMT output using a gated integrator (Stanford Research SR250). The integrator output was digitized by a 12 bit ADC (Measurement Computing USB-1208FS), and passed to a computer for analysis. Typically, the signal was averaged over 20 laser shots at each step in wavelength (typically 0.003 nm). Data collection and laser wavelength control was achieved using LABVIEW software.

Results and Discussion

Fluorescence Excitation Spectroscopy. In our initial communication, we reported a rotational analysis of one :CHI band at 13 638 cm^{-1}, which, on the basis of a comparison with theoretical predictions,[102] was tentatively assigned as 2_0^3 or 2_0^4.[66] In this work, we have conducted extensive fluorescence excitation surveys for both :CHI and :CDI, extending down in frequency to the limit of our detection system and up in frequency to the limit of the Franck−Condon envelope. The overall appearance of the :CHI spectrum is very similar to that of :CHBr;[48] namely, the appearance of closely spaced sets of bands assigned to members of the $2_0^{n-x}3_0^x$ progressions, with x = 0−3. The :CDI spectrum is similar; however, only two progressions were observed, with x = 0 and 1. Band positions of the 2_0^n progressions for both isotopomers were linearly extrapolated to a common origin near 10 500 cm^{-1} (Figure 1), confirming the assignment of the :CHI 13 638 cm^{-1} band as 2_0^4. The derived position of the electronic origin is within ~400 cm^{-1} of a theoretical prediction at the CASPT2(12,9) level.[102] In preliminary experiments at Brookhaven National Laboratory, Zhong Wang and Trevor Sears have observed a weak band near 10 517 cm^{-1} using LIF, which is very close to our predicted position of the origin band.[103] Further studies will be needed to confirm the position of the origin.

Rotationally resolved fluorescence excitation spectra obtained for 16 bands of :CHI and twelve bands of :CDI were analyzed using the PGOPHER simulation package of Colin Western.[104] Since the rotational constants of the ground state were not known, we first conducted a global fit that incorporated data from a number of cold bands (typically 4−5), each originating from the $\tilde{X}^1A'$ vibrationless level. In this fit the excited state term energies and rotational constants of both upper and lower states were varied. The ground state effective rotational constants determined in this manner [$\bar{B}_0'' = (B_0'' + C_0'')/2 = 0.32829(34)$ cm^{-1} (:CHI); $\bar{B}_0'' = 0.30171(13)$ cm^{-1} (:CDI)] were in good agreement with theoretical (equilibrium) values that we calculated at the B3LYP/Sadlej-pVTZ level [$\bar{B}_{\mathrm{eq}}'' = (B_{\mathrm{eq}}'' + C_{\mathrm{eq}}'')/2 = 0.3213$ cm^{-1} (:CHI); $\bar{B}_{\mathrm{eq}}'' = 0.2932$ cm^{-1} (:CDI)]. The ground state constants thus determined were fixed in all subsequent fits. Due to the limited number of rotational levels in the jet-cooled spectrum (T_{rot} ~25 K), the centrifugal distortion constant Δ_J was only rarely determinable. The fit parameters for all measured cold bands of :CHI and :CDI are respectively given in Tables 1 and 2. The trends observed in the rotational constants are very similar to those found for :CHBr.[48]

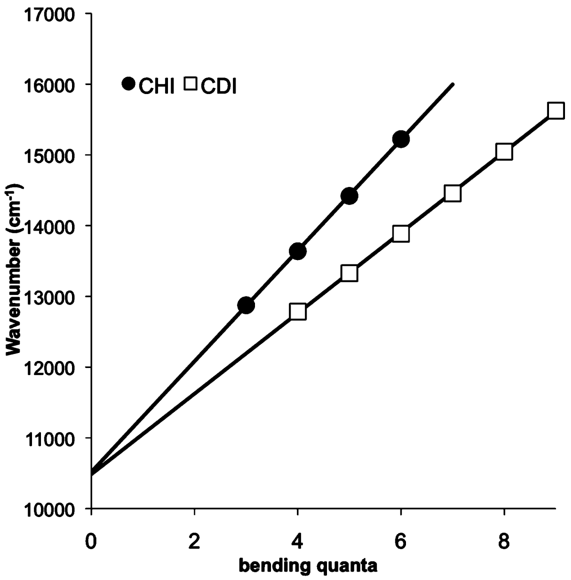

Figure 1. Band positions in the 2_0^n progressions of CHI and CDI (symbols). Lines represent linear fits to the data, which extrapolate to a common origin near 10 500 cm^{-1}.

TABLE 1: Fit Parameters (in cm^{-1}) for the :CHI ($\tilde{A}^1A''$) Bands Measured in This Work

band	T[a]	$(B' + C')/2$	Δ_J'	N[b]	σ[c]
2_0^3	12874.82(7)	0.3414(1)		28	0.05
$2_0^1 3_0^3$	13296.45(7)	0.3314(2)		16	0.02
$2_0^2 3_0^2$	13405.47(9)	0.3294(10)		6	0.03
$2_0^3 3_0^1$	13520.22(8)	0.3370(8)		10	0.05
2_0^4	13638.38(14)	0.3399(1)		20	0.03
$2_0^2 3_0^3$	14028.20(7)	0.3317(2)		20	0.04
$2_0^3 3_0^2$	14152.32(7)	0.3339(2)		23	0.05
$2_0^4 3_0^1$	14282.73(7)	0.3366(2)		17	0.03
2_0^5	14420.31(7)	0.3403(4)	$1.0(2) \times 10^{-5}$	20	0.02
$2_0^3 3_0^3$	14770.84(7)	0.3318(2)	$-3.0(2) \times 10^{-6}$	27	0.06
$2_0^4 3_0^2$	14910.83(7)	0.3340(1)		26	0.03
$2_0^5 3_0^1$	15058.71(7)	0.3424(9)	$1.3(1) \times 10^{-4}$	14	0.02
2_0^6	15223.50(7)	0.3385(2)		20	0.03
$2_0^4 3_0^3$	15523.67(7)	0.3291(2)		14	0.03
$2_0^5 3_0^2$	15680.97(7)	0.3325(5)		13	0.05
$2_0^6 3_0^1$	15852.08(7)	0.3356(1)		17	0.02

[a] One standard error in parentheses relative to the least significant digit. [b] Number of transitions included in the fit. [c] Standard deviation of the fit.

To further investigate the structure of the $\tilde{A}^1A''$ state, we carried out calculations at the CASSCF/Sadlej-pVTZ level using the Gaussian 98 program package.[105] The active space consisted of 10 electrons in 8 active orbitals, i.e., CASSCF(10,8). Optimization of the $\tilde{A}^1A''$ state at this level of theory yielded the following structural parameters: r_{CH} = 1.117 Å, r_{CI} = 2.040 Å, ∠HCI = 128.8°; and harmonic vibrational frequencies: (a) ω_1 = 2975 cm^{-1}, ω_2 = 819 cm^{-1}, ω_3 = 588 cm^{-1} for :CHI; (b) ω_1 = 2198 cm^{-1}, ω_2 = 624

TABLE 2: Fit Parameters (in cm^{-1}) for the :CDI ($\tilde{A}^1A''$) Bands Measured in This Work

band	T^a	$(B' + C')/2$	N^b	σ^c
2^4_0	12783.04(2)	0.3020(2)	15	0.02
$2^3_0 3^1_0$	12886.92(2)	0.2998(1)	28	0.01
2^5_0	13326.58(2)	0.3023(1)	21	0.03
$2^4_0 3^1_0$	13421.04(2)	0.2995(2)	19	0.03
2^6_0	13884.70(2)	0.3026(1)	23	0.02
$2^5_0 3^1_0$	13960.74(5)	0.3000(1)	25	0.02
2^7_0	14457.05(2)	0.3026(1)	20	0.02
$2^6_0 3^1_0$	14511.06(2)	0.3000(1)	22	0.03
2^8_0	15045.53(2)	0.3019(1)	22	0.01
$2^7_0 3^1_0$	15124.99(3)	0.2971(2)	19	0.04
2^9_0	15624.85(3)	0.2976(3)	18	0.04
$2^8_0 3^1_0$	15655.78(2)	0.3004(1)	22	0.02

[a] One standard error in parentheses relative to the least significant digit. [b] Number of transitions included in the fit. [c] Standard deviation of the fit.

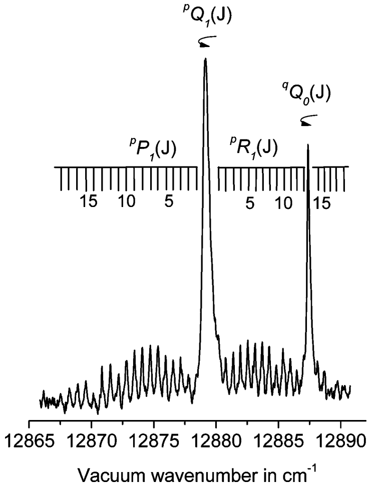

Figure 2. Fluorescence excitation spectrum of the CDI $2^3_0 3^1_0$ band. Rotational assignments are noted.

cm^{-1}, ω_3 = 565 cm^{-1} for :CDI. Optimized parameters for the ground state were r_{CH} = 1.141 Å, r_{CI} = 2.123 Å, and ∠HCI = 99.9°, similar to B3LYP/Sadlej-pVTZ predictions of r_{CH} = 1.127 Å, r_{CI} = 2.079 Å, and ∠HCI = 100.4°. Our calculated ground and excited state structural parameters are consistent with previous reports.[20,22,23,32] The bond angle increase of ~29° from $\tilde{X}^1A'$ to $\tilde{A}^1A''$ results in axis-tilting and the appearance of the nominally forbidden $^qQ_0$ sub-band (i.e., $K_a'' = 0 \rightarrow K_a' = 0$),[75] as illustrated in Figure 2. The position of this sub-band afforded a determination of the A rotational constant of the $\tilde{X}^1A'$ vibrationless level; A_0 = 15.5(1) cm^{-1} (:CHI), A_0 = 8.2(1) cm^{-1} (:CDI), in good agreement with theoretical values that we calculated at the B3LYP/Sadlej-pVTZ level; A_{eq} = 15.0 cm^{-1} (:CHI), A_{eq} = 8.3 cm^{-1} (:CDI).

On the basis of previous studies of :CHCl and :CHBr, and our estimate of $T_{00}(\tilde{A}-\tilde{X})$, we expect the barrier to linearity in the $\tilde{A}^1A''$ state of :CHI to lie below the position of the bands measured in this work. This is consistent with the fact that only sub-bands terminating in $K_a' = 0$ are observed in the spectra, as illustrated in Figure 2. Our calculations at the CASSCF(10,8)/Sadlej-pVTZ level indicate a barrier height of ~2200 cm^{-1} relative to the $\tilde{A}^1A''$ vibrationless level, similar to that found experimentally for :CHCl (~1920 cm^{-1}) and :CHBr (~1680 cm^{-1}).[48−50,52,74,95] An experimental determination of the barrier to linearity in the $\tilde{A}^1A''$ state will require the measurement of bands near the electronic origin.

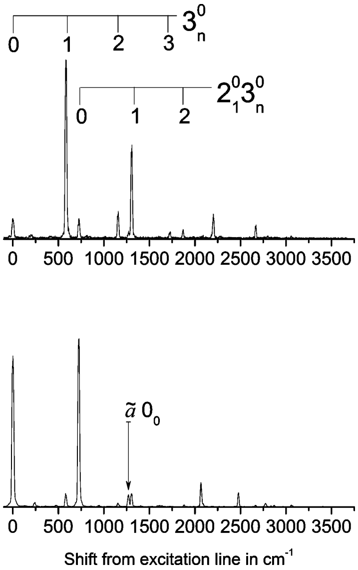

Figure 3. SVL emission spectra of CDI. The upper spectrum was obtained following excitation of the $2^6_0 3^1_0$ band, while the lower spectrum was obtained following excitation of the 2^7_0 band. Vibrational assignments are noted.

To estimate the C−I stretching frequency in the $\tilde{A}^1A''$ state, we performed a linear extrapolation to $n = 0$ of the difference in energies between members of the $2^n_0 3^1_0$ and 2^n_0 progressions with the same value of n. This yielded ν_3 = 665 cm^{-1} (:CHI) and 668 cm^{-1} (:CDI).

Single Vibronic Level Emission Spectroscopy. The analysis above conclusively shows that the spectrum observed for :CHI and :CDI is the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ system. However, this alone does not resolve the issue of the ground state multiplicity, since low-lying metastable states may be populated in the discharge. To investigate this issue, we used single vibronic level (SVL) emission spectroscopy. On the basis of previous results for the monohalocarbenes, particularly CHBr,[48,49,57,58,61,64] we expect that (a) the vibrational structure of $\tilde{X}^1A'$ will be severely perturbed at energies above the $\tilde{a}^3A''$ origin and (b) the bending levels of $\tilde{X}^1A'$ will be the most severely perturbed, due to larger vibrational overlaps with $\tilde{a}^3A''$ levels. Indeed, our results for CHI identify a regular vibrational progression in the C−I stretching mode (i.e., 3_n) extending up to n = 5, from which a harmonic frequency of 594.0(2) cm^{-1} and diagonal anharmonicity constant (i.e., x^0_{22}) of −3.12(4) cm^{-1} are derived. The former is in excellent agreement with a theoretical (B3LYP/Sadlej-pVTZ) prediction of 589 cm^{-1}. In contrast, the bending fundamental is found ~100 cm^{-1} below the B3LYP prediction, indicating a strong perturbation with a higher-lying state that we identify as the $\tilde{a}^3A''$ origin. These results confirm a singlet multiplicity for the ground state, and a deperturbation analysis based on a two level interaction between $\tilde{X}^1A'$ 2_1 and $\tilde{a}^3A''$ 0_0 gave a lower limit on ΔE_{ST} of 3.76 kcal mol^{-1}.

Spectra for :CDI (Figure 3) also show a regular progression in the C−I stretch (3_n) extending up to n = 4. In addition, the $2_1 3_n$ progression is observed, with n = 0−3. However, these are the only $\tilde{X}^1A'$ levels that can be straightforwardly assigned. Analysis of the C−I stretching states using the standard anharmonic oscillator treatment yields a harmonic C−I stretching frequency of 585.0(7) cm^{-1} and diagonal anharmonicity constant (x^0_{22}) of −3.4(2) cm^{-1}. The former is in good agreement with our calculations at the B3LYP/Sadlej-pVTZ level (575 cm^{-1}). The :CDI bending fundamental (i.e., 2_1) is found at 722 cm^{-1}, well below the position of the $\tilde{a}^3A''$ origin, and appears to be unperturbed on the basis of the regular appearance of the 2_13_n progression. In contrast, the vibrational structure at energies near and above the bending overtone (i.e., 2_2) is severely perturbed, and very few firm assignments can be made above this energy.

In the region centered around 1400 cm^{-1}, where only the $\tilde{X}^1A'$ 2_2 level is expected, three levels are observed, at 1268, 1586, and 1610 cm^{-1} (Figure 3). By analogy with :CHI, two of these are $\tilde{X}^1A'2_2$ and $\tilde{a}^3A''$ 0_0. The third, at 1586 or 1610 cm^{-1}, must be a higher lying level that is shifted down by perturbation. Our analysis assumes a two-level interaction between $\tilde{X}^1A'$ 2_2 and $\tilde{a}^3A''$ 0_0, the lower energy member of the perturbed pair lying at 1268 cm^{-1}, and the upper member at 1586 or 1610 cm^{-1}. Using the formulas derived from two level perturbation theory, we calculated the positions of the unperturbed levels and the vibronic coupling matrix elements for both cases. This analysis required an estimate of the unperturbed position of $\tilde{X}^1A'2_2$; for this we used the observed bending fundamental frequency and estimated the diagonal anharmonicity constant by scaling the value obtained for :CDBr[49] by the ratio of fundamental bending frequencies. This analysis shows that the zeroth-order position of the $\tilde{a}^3A''$ 0_0 level is nearly degenerate with that of $\tilde{X}^1A'2_2$ and, using a value of 1586 cm^{-1} for the upper member, we derive a lower limit on $T_{00}(\tilde{A}-\tilde{X})$ of 4.1 kcal mol^{-1}. The derived vibronic matrix element for the $\tilde{X}^1A'2_2-\tilde{a}^3A''$ 0_0 interaction is ~160 cm^{-1}.

To aid in making assignments, we carried out calculations of the $\tilde{a}^3A''$ state at the B3LYP/Sadlej-pVTZ level. Optimization at this level of theory yielded the following structural parameters: $r_{CH} = 1.100$ Å, $r_{CI} = 2.012$ Å, $\angle HCI = 129.7°$. Calculated harmonic vibrational frequencies were (a) $\omega_1 = 3139$ cm^{-1}, $\omega_2 = 794$ cm^{-1}, and $\omega_3 = 642$ cm^{-1} for :CHI, and (b) $\omega_1 = 2318$ cm^{-1}, $\omega_2 = 648$ cm^{-1}, and $\omega_3 = 576$ cm^{-1} for :CDI. Our calculated parameters are consistent with previous reports.[20,22,23,32]

Combined results from the SVL emission spectra of :CHI and :CDI show that $T_{00}(\tilde{A}-\tilde{X}) \geq 4.1$ kcal mol^{-1}. This lower bound is in excellent agreement with a variety of theoretical predictions. However, it is in poor agreement with the negative ion photoelectron spectroscopy measurements of Lineberger and co-workers.[46] The observed vibrational levels for :CHI and :CDI derived from SVL emission spectroscopy are given in Table 3 with assignments.

Conclusions

We have measured fluorescence excitation and emission spectra of the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ system of :CHI and the deuterated isotopomer :CDI. Due to similar bending and C−I stretching frequencies in the upper state, fluorescence excitation spectra of :CHI show polyads composed of members of the $2_0^{n-x}3_0^x$ progressions with $x = 0-3$; for :CDI, only progressions with $x = 0, 1$ are observed. Extrapolation of the 2_0^n term energies for both isotopomers to a common origin places the electronic origin of the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ system near 10 500 cm^{-1}, in good agreement with theoretical predictions. Preliminary experiments conducted at Brookhaven National Laboratories by Zhong Wang and Trevor Sears have identified a band at 10 517 cm^{-1} which may be the 0_0^0 band; future studies will seek to measure spectra of bands in this region to determine the origin frequency and the barrier to linearity in the $\tilde{A}^1A''$ state. Future work will also involve a search for C−H (C−D) stretching states, which have been observed in the $\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ systems of the other monohalocarbenes.

To investigate the controversial issue of the ground state multiplicity of :CHI, we measured single vibronic level emission spectra from many $\tilde{A}^1A''$ levels, which show conclusively that the ground state is a singlet. At energies above the $\tilde{a}^3A''$ origin, the spin−orbit mixing is so severe that few vibrational assignments can be made. Analysis of the emission spectra provides a lower limit on $T_{00}(\tilde{A}-\tilde{X})$ of 4.1 kcal mol^{-1}, in excellent agreement with theoretical predictions. Future work will focus on a more detailed deperturbation analysis of the emission spectra to obtain a more accurate value for $T_{00}(\tilde{A}-\tilde{X})$ and determine the purely electronic spin−orbit coupling matrix element.

TABLE 3: Derived $\tilde{X}^1A'$ Vibrational Levels for :CHI and :CDI with Tentative Assignments

:CHI		:CDI	
term energy[a]	assignment	term energy	assignment
0	0_0	0	0_0
591(2)	3_1	583(3)	3_1
948(2)	2_1	723(2)	2_1
1176(2)	3_2	1156(2)	3_2
1407(2)	$\tilde{a}$ 0_0	1268(2)	$\tilde{a}$ 0_0
1582(2)	2_13_1	1304(2)	2_13_1
1754(2)	3_3	1585(2)	
1975(2)	$\tilde{a}$ 3_1 ?	1610(2)	
2070(2)	2_2 ?	1724(2)	3_3
2218(3)	2_13_2	1876(6)	2_13_2
2326(3)	3_4	2066(2)	
2584(7)		2200(2)	
2852(2)		2286(4)	3_4
2892(2)	3_5	2477(2)	
		2666(3)	
		2776(2)	
		2800(4)	
		3058(3)	

[a] In cm^{-1}, one standard error in parentheses relative to least significant digit.

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References and Notes

(1) Moss, R. A.; Platz, M. S.; Jones, M., Jr. *Reactive Intermediate Chemistry*; Wiley-Interscience: Hoboken, NJ, 2004.
(2) Harrison, J. F.; Allen, L. C. *J. Am. Chem. Soc.* **1969**, *91*, 807.
(3) Harrison, J. F. *J. Am. Chem. Soc.* **1971**, *93* (17), 4112–19.
(4) Staemmler, V. *Theor. Chim. Acta* **1974**, *35* (4), 309–27.
(5) Takabe, T.; Takahashi, M.; Fukutome, H. *Prog. Theor. Phys.* **1976**, *56* (2), 689–702.
(6) Bauschlicher Jr., C. W.; Jr.; Schaefer, H. F., III.; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99* (22), 7106–10.
(7) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100* (5), 1333–8.
(8) Ha, T.; Gremlich, H. U.; Buhler, R. E. *Chem. Phys. Lett.* **1979**, *65*, 16.
(9) Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103* (17), 5049–52.
(10) Scuseria, G. E.; Duran, M.; Maclagan, R. G. A. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108* (12), 3248–53.
(11) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1987**, *91* (18), 4651–2.
(12) Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* **1988**, *88* (3), 1752–63.
(13) Shin, S. K.; Goddard, W. A., III.; Beauchamp, J. L. *J. Phys. Chem.* **1990**, *94* (18), 6963–9.
(14) Gutsev, G. L.; Ziegler, T. *J. Phys. Chem.* **1991**, *95*, 7220.
(15) Irikura, K. K.; Goddard, W. A., III.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114* (1), 48–51.
(16) Vetter, R.; Reuter, W.; Peyerimhoff, S. D. *Chem. Phys.* **1992**, *161* (3), 379–92.

(17) Russo, N.; Sicilia, E.; Toscano, M. *J. Chem. Phys.* **1992**, *97* (7), 5031–6.

(18) Gobbi, A.; Frenking, G. *Bull. Chem. Soc. Jpn.* **1993**, *66* (11), 3153–65.

(19) Gobbi, A.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1993**, *14*, 1162–4.

(20) Russo, N.; Sicilia, E.; Toscano, M. *Chem. Phys. Lett.* **1993**, *213* (3−4), 245–9.

(21) Cai, Z. L. *J. Phys. Chem.* **1993**, *97* (32), 8399–402.

(22) Garcia, V. M.; Castell, O.; Reguero, M.; Caballol, R. *Mol. Phys.* **1996**, *87* (6), 1395–1404.

(23) Worthington, S. E.; Cramer, C. J. *J. Phys. Org. Chem.* **1997**, *10* (10), 755–67.

(24) Poutsma, J. C.; Paulino, J. A.; Squires, R. R. *J. Phys. Chem. A* **1997**, *101* (29), 5327–36.

(25) Knepp, P. T.; Scalley, C. K.; Bacskay, G. B.; Kable, S. H. *J. Chem. Phys.* **1998**, *109*, 2220–2232.

(26) Vargas, R.; Galvan, M.; Vela, A. *J. Phys. Chem. A* **1998**, *102* (18), 3134–40.

(27) Havlas, Z.; Michl, J. *Collect. Czech. Chem. Commun.* **1998**, *63* (9), 1485–97.

(28) Schwartz, M.; Marshall, P. *J. Phys. Chem. A* **1999**, *103* (39), 7900–06.

(29) Das, D.; Whittenburg, S. L. *THEOCHEM* **1999**, *492*, 175–86.

(30) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64* (19), 7061–66.

(31) Hu, C.-H. *Chem. Phys. Lett.* **1999**, *309* (1−2), 81–89.

(32) Hajgato, B.; Nguyen, H. M. T.; Veszpremi, T.; Nguyen, M. T. *Phys. Chem. Chem. Phys.* **2000**, *2* (22), 5041–45.

(33) Sendt, K.; Bacskay, G. B. *J. Chem. Phys.* **2000**, *112* (5), 2227–38.

(34) Sendt, K.; Schmidt, T. W.; Bacskay, G. B. *Int. J. Quantum Chem.* **2000**, *76* (3), 297–305.

(35) Scott, A. P.; Platz, M. S.; Radom, L. *J. Am. Chem. Soc.* **2001**, *123* (25), 6069–6076.

(36) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117* (10), 4694–4708.

(37) McKee, M. L.; Michl, J. *J. Phys. Chem. A* **2002**, *106*, 8495–8497.

(38) Kalemos, A.; Dunning, T. H.; Mavridis, A.; Harrison, J. F. *Can. J. Chem.* **2004**, *82*, 684–693.

(39) Olah, J.; De Proft, F.; Veszpremi, T.; Geerlings, P. *J. Phys. Chem. A* **2004**, *108* (3), 490–99.

(40) Guss, J. S.; Bacskay, G. B.; Kable, S. H. *Chem. Phys. Lett.* **2005**, *405*, 258–264.

(41) Chau, F.-t.; Mok, D. K. W.; Lee, E. P. F.; Dyke, J. M. *Chem. Phys. Chem.* **2005**, *6* (10), 2037–45.

(42) Tarczay, G.; Miller, T. A.; Czako, G.; Csaszar, A. G. *Phys. Chem. Chem. Phys.* **2005**, *7* (15), 2881–93.

(43) Dyke, J. M.; Lee, E. P. F.; Mok, D. K. W.; Chau, F.-t. *Chem. Phys. Chem.* **2005**, *6* (10), 2046–59.

(44) Yu, H.-G.; Sears, T. J.; Muckerman, J. T. *Mol. Phys.* **2006**, *104*, 47–53.

(45) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89* (9), 5442–53.

(46) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1992**, *96* (3), 1130–41.

(47) Schwartz, R. L.; Davico, G. E.; Ramond, T. M.; Lineberger, W. C. *J. Phys. Chem. A* **1999**, *103* (41), 8213–21.

(48) Deselnicu, M.; Tao, C.; Mukarakate, C.; Reid, S. A. *J. Chem. Phys.* **2006**, *124*, 134302/11.

(49) Tao, C.; Deselnicu, M.; Mukarakate, C.; Reid, S. A. *J. Chem. Phys.* **2006**, *125*, 094305/9.

(50) Tao, C.; Mukarakate, C.; Reid, S. A. *J. Chem. Phys.* **2006**, *124*, 224314/11.

(51) Tao, C.; Deselnicu, M.; Fan, H.; Mukarakate, C.; Ionescu, I.; Reid, S. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 707–713.

(52) Tao, C.; Mukarakate, C.; Reid, S. A. *J. Mol. Spectrosc.* **2007**, *241*, 136–142.

(53) Tao, C.; Mukarakate, C.; Brusse, D.; Mishchenko, Y.; Reid, S. A. *J. Mol. Spectrosc.* **2007**, *241*, 180–185.

(54) Tao, C.; Mukarakate, C.; Reid, S. A. *J. Mol. Spectrosc.* **2007**, *246*, 113–117.

(55) Tao, C.; Mukarakate, C.; Reid, S. A. *J. Mol. Spectrosc.* **2007**, *241*, 143–150.

(56) Chen, C.-W.; Tsai, T.-C.; Chang, B.-C. *Chem. Phys. Lett.* **2001**, *347*, 73–78.

(57) Tsai, T.-S.; Chen, C.-W.; Chang, B.-C. *J. Chem. Phys.* **2001**, *115*, 766–771.

(58) Chen, C.-W.; Tsai, T.-C.; Chang, B.-C. *J. Mol. Spectrosc.* **2001**, *209*, 254–258.

(59) Lee, C.-L.; Liu, M.-L.; Chang, B.-C. *J. Chem. Phys.* **2002**, *117*, 3263–3268.

(60) Liu, M.-L.; Lee, C.-L.; Bezant, A.; Tarczay, G.; Clark, R. J.; Miller, T. A.; Chang, B.-C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1353–1358.

(61) Lee, C.-L.; Liu, M.-L.; Chang, B.-C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3859–3863.

(62) Lin, C.-S.; Chen, Y.-E.; Chang, B.-C. *J. Chem. Phys.* **2004**, *121*, 4164–4170.

(63) Hsu, H.-J.; Chang, W.-Z.; Chang, B.-C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2468–2473.

(64) Chang, W.-Z.; Hsu, H.-J.; Chang, B.-C. *Chem. Phys. Lett.* **2005**, *413*, 25–30.

(65) Fan, H.; Mukarakate, C.; Deselnicu, M.; Tao, C.; Reid, S. A. *J. Chem. Phys.* **2005**, *123*, 014314/7.

(66) Tao, C.; Ebban, C.; Ko, H.-T.; Reid, S. A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6090–6092.

(67) Suzuki, T.; Hirota, E. *J. Chem. Phys.* **1988**, *88* (11), 6778–84.

(68) Tao, C.; Mukarakate, C.; Judge, R. H.; Reid, S. A. *J. Chem. Phys.* **2008**, *128*, 171101/4.

(69) Tao, C.; Mukarakate, C.; Terranova, Z.; Ebban, C.; Judge, R. H.; Reid, S. A. *J. Chem. Phys.* **2008**, *129*, 104309/8.

(70) Mukarakate, C.; Tao, C.; Jordan, C. D.; Polik, W. F.; Reid, S. A. *J. Phys. Chem. A* **2008**, *112*, 466–471.

(71) Field, R. W. *Bull. Am. Phys. Soc.* **1980**, *25* (3), 160–160.

(72) Field, R. W. *Abstr. Pap. Am. Chem. Soc.* **1981**, *181* (Mar), 61-PHYS.

(73) Kittrell, C.; Abramson, E.; Kinsey, J. L.; Mcdonald, S. A.; Reisner, D. E.; Field, R. W.; Katayama, D. H. *J. Chem. Phys.* **1981**, *75* (5), 2056–2059.

(74) Yu, H.-G.; Gonzalez-Lezana, T.; Marr, A. J.; Muckerman, J. T.; Sears, T. J. *J. Chem. Phys.* **2001**, *115*, 5433–5444.

(75) Lin, A.; Kobayashi, K.; Yu, H.-G.; Hall, G. E.; Muckerman, J. T.; Sears, T. J.; Merer, A. J. *J. Mol. Spectrosc.* **2002**, *214*, 216–224.

(76) Yu, H.-G.; Muckerman, J. T.; Sears, T. J. *J. Chem. Phys.* **2002**, *116* (4), 1435–1442.

(77) Chang, B.-C.; Guss, J. S.; Sears, T. J. *J. Mol. Spectrosc.* **2003**, *219*, 136–144.

(78) Clouthier, D. J.; Karolczak, J. *J. Phys. Chem.* **1989**, *93* (22), 7542–4.

(79) Clouthier, D. J.; Karolczak, J. *J. Chem. Phys.* **1991**, *94* (1), 1–10.

(80) Marr, A. J.; North, S. W.; Sears, T. J.; Ruslen, L.; Field, R. W. *J. Mol. Spectrosc.* **1998**, *188*, 68–77.

(81) Fan, H.; Ionescu, I.; Annesley, C.; Reid, S. A. *Chem. Phys. Lett.* **2003**, *378*, 548–552.

(82) Fan, H.; Ionescu, I.; Annesley, C.; Cummins, J.; Bowers, M.; Reid, S. A. *J. Mol. Spectrosc.* **2004**, *225*, 43–47.

(83) Ionescu, I.; Fan, H.; Annesley, C.; Xin, J.; Reid, S. A. *J. Chem. Phys.* **2004**, *120*, 1164–1167.

(84) Fan, H.; Ionescu, I.; Xin, J.; Reid, S. A. *J. Chem. Phys.* **2004**, *121*, 8869–8873.

(85) Ionescu, I.; Fan, H.; Ionescu, E.; Reid, S. A. *J. Chem. Phys.* **2004**, *121*, 8874–8879.

(86) Fan, H.; Ionescu, I.; Annesley, C.; Cummins, J.; Bowers, M.; Xin, J.; Reid, S. A. *J. Phys. Chem. A* **2004**, *108*, 3732–3738.

(87) Ionescu, E.; Reid, S. A. *J. Mol. Struct. THEOCHEM* **2005**, *725*, 45–53.

(88) Mukarakate, C.; Mishchenko, Y.; Brusse, D.; Tao, C.; Reid, S. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4320–4326.

(89) Tao, C.; Reid, S. A.; Schmidt, T. W.; Kable, S. H. *J. Chem. Phys.* **2007**, *126*, 051105/4.

(90) Richmond, C. A.; Tao, C.; Mukarakate, C.; Fan, H.; Nauta, K.; Schmidt, T. W.; Kable, S. H.; Reid, S. A. *J. Phys. Chem. A* **2008**, *112*, 11355–11362.

(91) Chang, B.-C.; Sears, T. J. *J. Chem. Phys.* **1995**, *102*, 6347–6353.

(92) Chang, B.-C.; Sears, T. J. *J. Mol. Spectrosc.* **1995**, *173*, 391–403.

(93) Chang, B.-C.; Sears, T. J. *J. Chem. Phys.* **1996**, *105*, 2135–40.

(94) Chang, B.-C.; Fei, R.; Sears, T. J. *J. Mol. Spectrosc.* **1997**, *183*, 341–346.

(95) Marr, A. J.; Sears, T. J. *J. Mol. Spectrosc.* **1999**, *195*, 367–370.

(96) Marr, A. J.; Sears, T. J. *Mol. Phys.* **1999**, *99*, 185–193.

(97) Hall, G. E.; Sears, T. J.; Yu, H.-G. *J. Mol. Spectrosc.* **2006**, *235*, 125–131.

(98) Wang, Z.; Bird, R. G.; Yu, H.-G.; Sears, T. J. *J. Chem. Phys.* **2006**, *124*, 074314/7.

(99) Chang, B.-C.; Costen, M. L.; Marr, A. J.; Ritchie, G.; Hall, G. E.; Sears, T. J. *J. Mol. Spectrosc.* **2000**, *202*, 131–143.

(100) Choe, J. I.; Tanner, S. R.; Harmony, M. D. *J. Mol. Spectrosc.* **1989**, *138* (2), 319–31.

(101) Xu, S.; Beran, K. A.; Harmony, M. D. *J. Phys. Chem.* **1994**, *98*, 2742–2743.

(102) Drake, S. A.; Standard, J. M.; Quandt, R. W. *J. Phys. Chem. A* **2002**, *106* (7), 1357–64.

(103) Wang, Z.; Sears, T. J. Unpublished work, 2009.

(104) Western, C. M. *PGOPHER, a Program for Simulating Rotational Structure*, http://pgopher.chm.bris.ac.uk.

(105) Frisch, M. J.; , G. W. T., Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 2001.

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