

## Laser Spectroscopy of a Halocarocation in the Gas Phase: $\text{CH}_2\text{I}^+$

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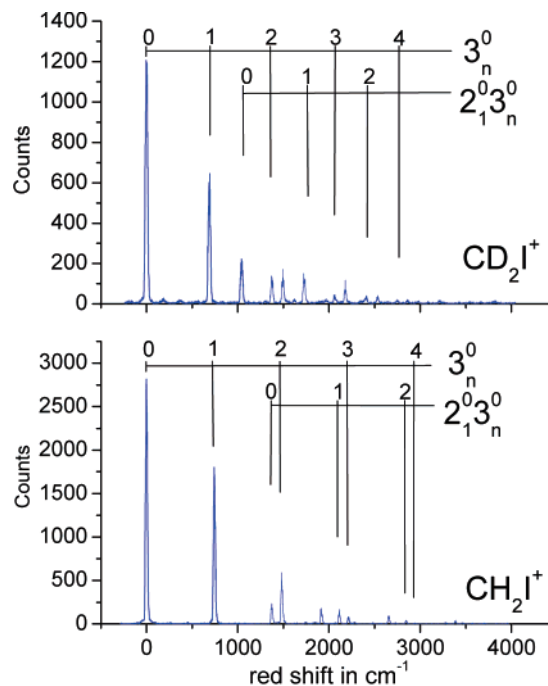
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Reactive carbocation intermediates are encountered in a myriad of industrially and physiologically important processes, and while the development of methods to generate persistent carbocations in condensed phases led to a flurry of studies culminating in the 1994 Nobel Prize in Chemistry,<sup>1</sup> these important ions have regrettably resisted gas-phase spectroscopic analysis. For example, the infrared spectrum of  $\text{CH}_3^+$  was not obtained until 1985!<sup>2</sup> To this day, little structural information exists for simple carbocations, such as  $\text{CH}_2\text{X}^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). These species are observed and their reactions studied with mass spectrometric techniques,<sup>3</sup> and many theoretical studies have been undertaken to predict their structure and spectroscopic properties,<sup>4</sup> yet experimental proof is lacking. In this communication, we report the first gas-phase observation of the electronic spectrum of a halocarocation,  $\text{CH}_2\text{I}^+$ , which was generated using pulsed discharge techniques and was detected using laser spectroscopy. We believe that this initial detection will open new avenues for study of the structure and reactivity of these important species.

The monohalocarocation  $\text{CH}_2\text{I}^+$  was produced using gas phase pulsed discharge supersonic jet techniques that have been described in detail.<sup>5</sup> A stable precursor,  $\text{CH}_2\text{I}_2$  (Aldrich, 99.5% stated purity), seeded in high purity helium at a mole fraction of  $\sim 1\%$ , was subjected to a high voltage discharge pulse of amplitude +1000 V and 700  $\mu\text{s}$  duration. The discharge products expanded into vacuum, leading to significant rotational cooling ( $T_{\text{rot}} \sim 20$  K), and were intersected by the output of a pulsed tunable laser system. The resulting fluorescence was collected, filtered, and detected by a photomultiplier tube, and the signal was passed to a computer for analysis. Wavelength resolved spectra were obtained using a 0.3 m spectrograph with a gated intensified CCD detector. In comparison with previous studies of neutral molecules generated from the same source,<sup>5</sup> the discharge conditions were more critical, and the signal was optimized at a significantly shorter delay setting, which provided the first indication that the carrier of the spectrum was an ion. To confirm its identity, we carried out experiments with diiodomethane- $d_2$  (Cambridge Isotope labs, >99% atom D).

Using the  $\text{CH}_2\text{I}_2$  precursor, we initially obtained fluorescence excitation spectra in the region of 580–660 nm, which showed a prominent series of (partially) rotationally resolved bands spaced at  $\sim 570$   $\text{cm}^{-1}$ . The origin, at  $\sim 15\,180$   $\text{cm}^{-1}$ , shifted to  $\sim 15\,288$   $\text{cm}^{-1}$  when the precursor was replaced with diiodomethane- $d_2$ , and the band system disappeared when the precursor was changed to  $\text{CH}_3\text{I}$  or  $\text{CH}_2\text{ICl}$ . Emission spectra were obtained from the observed bands, and examples are given in Figure 1; these show two prominent progressions, in addition to several weaker features. We fit the term energies in these two progressions to a two-mode Dunham expansion to derive an initial set of vibrational parameters,<sup>5</sup> and the experimental harmonic frequencies are listed in Table 1. These were compared with literature or calculated<sup>6</sup> (B3LYP/6-311G\*\*) frequencies for a variety of candidates, including CHI,  $\text{CH}_2\text{I}$ ,  $\text{CHI}_2$ , and their corresponding cations and anions, and  $\text{CH}_2\text{I}_2^+$ . As shown in Table 1, excellent agreement was obtained with



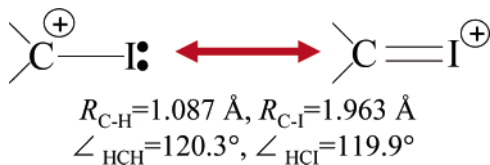
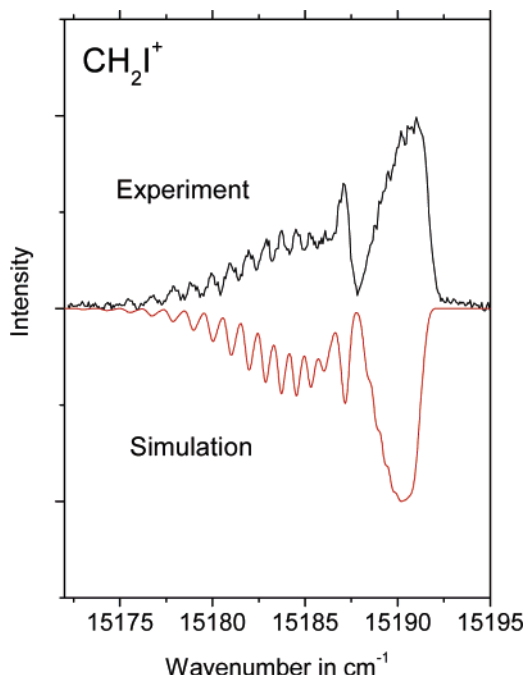
**Figure 1.** Single vibronic level emission spectra of  $\text{CD}_2\text{I}^+$  (top) and  $\text{CH}_2\text{I}^+$  obtained following excitation of their origin bands. Progressions involving two fundamentals are observed, as marked in the figure.

calculated  $\text{CH}_2\text{I}^+$  frequencies for  $\nu_2$  ( $\text{CH}_2$  scissor) and  $\nu_3$  (C–I stretch), and the calculated frequency shifts for these modes upon deuteration were well reproduced (Table 1). Other candidates were eliminated based on the following considerations: (1) there is no known electronic transition in the visible for the iodomethyl radicals, and the literature vibrational frequencies were not in agreement;<sup>7</sup> (2) the calculated frequencies of neutral and ionic CHI and the iodomethyl ions were not in agreement; (3)  $\text{CH}_2\text{I}_2^+$  has a weak electronic transition near 570 nm, and DFT calculations predict a vibrational fundamental near 755  $\text{cm}^{-1}$ ;<sup>8</sup> however, the predicted shift in this mode upon (double) deuteration is 3 times larger than we observe (i.e.,  $-24$  vs  $-8\%$ ).

To confirm our assignment of the spectral carrier to  $\text{CH}_2\text{I}^+$ , we modeled the rotational structure in the excitation spectrum. The ground state of  $\text{CH}_2\text{I}^+$  is  $\tilde{X}^1A_1$ , and calculations at the CIS/6-311G\*\* level show no singlet excited states with transition energies in the visible region; however, a triplet  $A_1$  state is predicted. Although our laser resolution ( $\sim 0.2$   $\text{cm}^{-1}$ ) was insufficient to achieve complete rotational resolution, the band type could nonetheless be determined, which identified the symmetry of the upper state. We optimized the geometry at the B3LYP/6-311G\*\* level, yielding the structural parameters shown in Figure 2. The calculated ground state rotational constants (in  $\text{cm}^{-1}$ ;  $A = 9.417$ ,  $B = 0.318$ ,  $C = 0.307$ ) were used in simulations which incorporated the 3:1 ortho:para nuclear spin weighting and varied the upper state constants to obtain the best fit. These simulations (Figure 3) show good

**Table 1.** Comparison of Experiment and Theory for the Vibrational Frequencies of CH<sub>2</sub>I<sup>+</sup> Isotopomers in the  $\tilde{X}^1A_1$  State

	method	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(a_1)$	$\omega_4(b_1)$	$\omega_5(b_2)$	$\omega_6(b_2)$
CH <sub>2</sub> I <sup>+</sup>	B3LYP/6-311G**	3116.8	1424.8	753.3	1017.3	3254.8	899.2
	experiment (this work)		1398(4)	755(1)			
CD <sub>2</sub> I <sup>+</sup>	B3LYP/6-311G**	2254.2	1075.3	695.5	793.1	2431.8	671.2
	experiment (this work)		1062(4)	696(2)			
ratio (d <sub>2</sub> /h <sub>2</sub> )	B3LYP/6-311G**	0.72	0.76	0.92	0.78	0.75	0.75
	experiment (this work)		0.76(1)	0.92(1)			

**Figure 2.** Resonance structures for the CH<sub>2</sub>I<sup>+</sup> carbocation and optimized ground state geometrical parameters at the B3LYP/6-311G\*\* level.**Figure 3.** Comparison of experimental (upper) and simulated excitation spectra for the origin band of CH<sub>2</sub>I<sup>+</sup>. The simulation is based on calculated ground state rotational constants and assumes an *a*-type rotational contour and rotational temperature of 17 K.

agreement with an *a*-type contour, indicating that the upper state has *A*<sub>1</sub> electronic symmetry. We thus assign this transition to  $^3A_1 \leftarrow \tilde{X}^1A_1$ . The intensity of this transition will be significantly weaker for the lighter monohalocarboanions, which may explain why it has not previously been observed. It must be noted, however, that the simulation shown in Figure 3 did not include the effects of electron spin in the upper state, and therefore, we cannot at this time rule out the possibility that the excited state is a singlet.

The derived frequencies for  $\nu_2$  and  $\nu_3$  (Table 1) and optimized geometrical parameters (Figure 2) are similar to those calculated for *iso*-CH<sub>2</sub>I–I,<sup>8,9</sup> which is formed from CH<sub>2</sub>I<sub>2</sub> photolysis in condensed phase environments via geminate recombination. As previously noted,<sup>9</sup> the charge distribution of the CH<sub>2</sub>I moiety in

*iso*-CH<sub>2</sub>I–I is similar to that of CH<sub>2</sub>I<sup>+</sup>. Also, the calculated C–I bond lengths (Figure 2 and ref 4) are significantly shorter than those typical for singly bonded species (~2.16 Å),<sup>10</sup> indicating that the C–I bond in CH<sub>2</sub>I<sup>+</sup> has significant double bond character. This is also reflected in the large C–I stretching frequency.

Finally, a photodissociation study of alkyl iodide cations proposed that (vibrationally hot) CH<sub>2</sub>I<sup>+</sup> formed from CH<sub>2</sub>I<sub>2</sub> by electron impact can be photodissociated to CH<sub>2</sub><sup>+</sup> throughout the visible region.<sup>11</sup> Using literature values for the heats of formation,<sup>12</sup> we calculate an enthalpy change  $\Delta H^\circ(298) = 478 \text{ kJ mol}^{-1}$  for the reaction: CH<sub>2</sub>I<sup>+</sup> → CH<sub>2</sub><sup>+</sup> + I. This corresponds to an appearance threshold (wavelength) of ~250 nm. Clearly, this channel is not accessible at the wavelengths used in this study, consistent with the observation of emission from the upper state. Further high-resolution studies of this band system and the ultraviolet spectrum of this cation are being actively pursued.

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**Supporting Information Available:** Tables of assigned vibrational term energies and Dunham fit parameters for the ground states of both isotopomers, parameters used in the simulation shown in Figure 3, and complete ref 6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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