Fourier transform microwave and millimeter-wave spectroscopy of the CH₂I radical ($^2B_1$)

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Interest & Aim
- Limited number of experimental (& theoretical) studies:
  - first identified by matrix infrared spectroscopy
  - one UV band observed by photoelectron spectroscopy
- also detected in emission by infrared spectroscopy
- recently: investigation of reaction mechanisms of Cl with CH₂I²

No high-resolution spectroscopic detection in the gas-phase reported thus far

Atmospheric interest:
- CH₂X (X=Cl, Br & I) radicals may have important implications in ozone depletion processes

Spectroscopic interest:
- complete the high-resolution studies in the microwave and millimeterwave regions of the CH₂X series for structural comparison (geometry and electronic configuration)

Empirical Prediction of the Hyperfine Interaction Constants of Iodine (I² = 5/2) (a necessity before conducting the experiments)

- Fermi-contact term a_F (measure the s-character of the unpolarized electron on the halogen): a_F/A² = atomic value for iodine = 41600 MHz
- Magnetic dipole-dipole interaction terms T_B: T = (T_{aa} + T_{bb}) with T = T_B for a σ-radical in the ²B₁ state

Using a spin density on the halogen similar to that in CH₂I2 & CH₂Br (-16%): T = 0.16 * (2/5 F₂entire) x Z = 260 MHz (P=atomic I=2031 MHz)

- Quadrupole coupling constants:
  \[ \chi(CH₂I) = 1934 MHz \Rightarrow scaling from CH₂Br, \chi(CH₂I) is predicted to be -1740 MHz \]
  \[ \chi_{bb} = +1088 MHz \text{ (scaled from } \chi_{aa}) \]

The Experiments

1. FTMW (Shizuoka University):
   - Precursors: CH₂I₂ or CH₂I
   - Backing pressure: 1.5 atm (Ar)
   - Pulsed discharge: 1.2 kV

   - CH₂I (even K)

2. Millimeter-wave (Lab. PhLAM, Lille 1 University):
   - Precursors: CH₂I or CH₂I₂ reacting with atomic Cl (for H or I abstraction reaction)
   - Temperature: partial cooling of the absorption cell by liquid nitrogen flow
   - Detected-by-products: stable: CH₂I₂CI (CH₂I₂ + CI), ICI, CH₂CI; transient: CH₂I₂(CH₂I₂ + CI)

Observations & Results

- Calculations:
  - predictions & least-squares analysis made with H.M. Pickett’s SPFIT & SPACAT
  - 32 parameters determined (including nuclear spin-rotation constants, not shown)
  - \( \chi_{aa} = 30 \text{ kHz} \)

- Spectra measured:
  - FTMW spectroscopy:
    - 73 hyperfine components between 17-38 GHz
    - hyperfine structure due to the hydrogen and iodine fully resolved
    - no splitting observed for the para-species (odd K): the G.S. is \( ^1I^b \), meaning the radical is planar in its ground vibrational state
  - MWM spectroscopy:
    - \( 12 \leq N^b = 35, K' \leq 6 \) between 200 - 610 GHz
    - hyperfine structure due to iodine nuclear spin partly resolved

<table>
<thead>
<tr>
<th>Constant (MHz)</th>
<th>Predicted</th>
<th>Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>273120</td>
<td>276676.7(3)</td>
</tr>
<tr>
<td>B + C</td>
<td>17343</td>
<td>17509.9416(40)</td>
</tr>
<tr>
<td>B - C</td>
<td>2420</td>
<td>283.1023(40)</td>
</tr>
<tr>
<td>( \epsilon_a )</td>
<td>-45000</td>
<td>-29409.791(12)</td>
</tr>
<tr>
<td>( \epsilon_a + \epsilon_b )</td>
<td>-8000</td>
<td>-717.720(39)</td>
</tr>
<tr>
<td>( \epsilon_a - \epsilon_b )</td>
<td>-12000</td>
<td>-1133.306(97)</td>
</tr>
<tr>
<td>a_F</td>
<td>+16.6</td>
<td>-15.8370(97)</td>
</tr>
<tr>
<td>T_{aa}</td>
<td>-148</td>
<td>-152.960(58)</td>
</tr>
<tr>
<td>( \frac{1}{2}(T_{bb} - T_{aa}) )</td>
<td>-93</td>
<td>-107.745(11)</td>
</tr>
<tr>
<td>( \frac{1}{2}(T_{ab} + T_{bb}) )</td>
<td>-1740</td>
<td>-1745.0225(34)</td>
</tr>
<tr>
<td>( \frac{1}{2}(2\epsilon_a - \epsilon_b) )</td>
<td>+109</td>
<td>+108.5243(37)</td>
</tr>
<tr>
<td>( \frac{1}{2}(2\epsilon_b - \epsilon_a) )</td>
<td>-60.208</td>
<td>-57.6056(9)</td>
</tr>
<tr>
<td>( \frac{1}{2}(T_{bb} - T_{aa}) )</td>
<td>-21.89</td>
<td>-20.7123(12)</td>
</tr>
<tr>
<td>( \frac{1}{2}(T_{bb} + T_{aa}) )</td>
<td>+7.02</td>
<td>+4.10(64)</td>
</tr>
</tbody>
</table>

CH₂I₂ values

\( a_F \) has been accurately determined, with its sign being unambiguously and surprisingly negative. \( a_F \) is positive in other CH₂X radicals.

Interpretation: spin polarization effect:
The sign results from a balance between \( \sigma- \) and \( \pi- \) spins on the halogen nucleus. The excess amount of \( \pi- \) spin on the halogen is clearly induced by spin polarization systematically decreases from 0.35% in CH₂F, 0.20% in CH₂Cl, 0.07% in CH₂Br, and 0.03% in CH₂I.

Conclusion:
- CH₂I radical \( (^2B_1, \text{ground state}) \) has been characterized in the gas phase for the first time by high-resolution molecular spectroscopy.
- The observed and hyperfine structures have been fully interpreted in terms of geometrical and electronic structure.
- These results complete the spectroscopic studies in the microwave and mmw regions of the CH₂I halogen-substituted radicals.