Fourier transform microwave and millimeter-wave spectroscopy of the CH_2I radical $(\tilde{X}\,^2B_1)$

S. Bailleux[1], P. Kania[1], H. Ozeki[2], T. Okabayashi[3], T. Matsumoto[3] and M. Tanimoto[4]

[1] Université Lille 1, Laboratoire PhLAM, CERLA, CNRS UMR 8523, F-59650 Villeneuve d'Ascq, France
2 Department of Environmental Science, Faculty of Science, Toho-University 2-2-1, Miyama, Funabashi 274-8510, Japan
[3] Center for Instrumental Analysis, Faculty of Science, Shizuoka University, Oya 836, Shizuoka 422-8529, Japan
[4] Department of Chemistry, Faculty of Science, Shizuoka University, Oya 836, Shizuoka 422-8529, Japan

Interest & Aim

➢ Limited number of experimental (& theoretical) studies:
- first identified by matrix infrared spectroscopy[1]
- one UV band observed by photoelectron spectroscopy[2]
- also detected in emission by infrared spectroscopy[3]
- recently: investigation of reaction mechanisms of Cl with CH_2I_2 [4]

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

➢ Atmospheric interest:
CH_2X (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 CH_2X series for structural comparison (geometry and electronic configuration)

Prediction of the Rotational Spectrum ($^2B_1$)

➢ Nearly planar structure calculated at the U-CCSD(T) level[5]:
R_{C-H} = 1.0775 Å R_{C-I} = 2.0500 Å $H\hat{C}I$ = 118.4°

slightly asymmetric prolate rotor: κ = -0.998

C_{2v} point group with a axis of symmetry ⇒ a-type spectrum

Dipole moment: 0.8 D

Rotational Constants /MHz: A_e = 279415 B_e = 8806 C_e = 8537

➢ Electron spin – rotation interaction constants:

scaling from CH_2Cl & CH_2Br, ε_{aa} & ε_{bb} should have large, negative values:

$\varepsilon_{aa} \approx$ - 45000 MHz

$\varepsilon_{bb} \approx$ - 1000 MHz

ε_{cc} should be small and positive for a planar π-radical (+200 MHz ?)
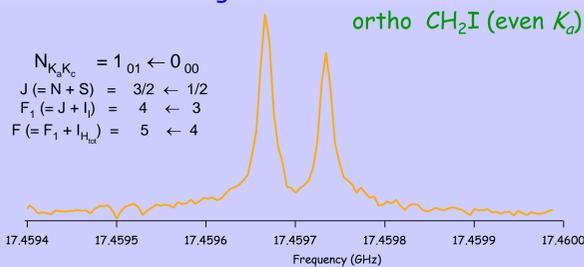
Empirical Prediction of the Hyperfine Interaction Constants of Iodine (I_I = 5/2) (a necessity before conducting the experiments!)

➢ Fermi-contact term a_F (measure the s-character of the unpaired electron on the halogen): a_F^I/A^I (A^I = atomic value for iodine = 41600 MHz)

CH_2F: a_F^F/A^F = 0.4 %; CH_2Cl: a_F^{Cl}/A^{Cl} = 0.2 %; CH_2Br: a_F^{Br}/A^{Br} = 0.08 % – Assuming a_F^I/A^I = 0.04 % , a_F^I was predicted to be positive: +16.6 MHz

➢ Magnetic dipole-dipole interaction terms T_{ii}: T_{cc} = - (T_{aa} + T_{bb}) with $T_{aa} \approx T_{bb}$ for a π-radical in the $^2B_1$ state

using a spin density on the halogen similar to that in CH_2Cl & CH_2Br (~16%): T_{cc} = 0.16 *(2/5 $P_{atomic\,I}$) x 2 ≈ +260 MHz ($P_{atomic\,I}$ = 2031 MHz)

➢ Quadrupole coupling constants:
$\chi(CH_3I)$ = -1934 MHz ⇒ scaling from CH_2Br, $\chi_{aa}(CH_2I)$ is predicted to be -1740 MHz

$\chi_{bb} \approx$ +1088 MHz (scaled from χ_{aa})

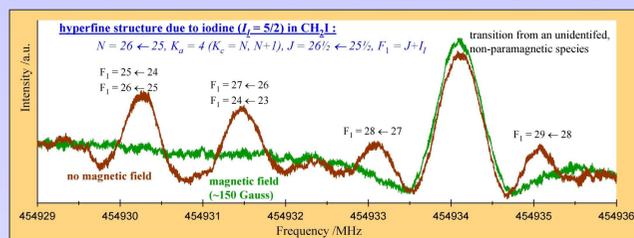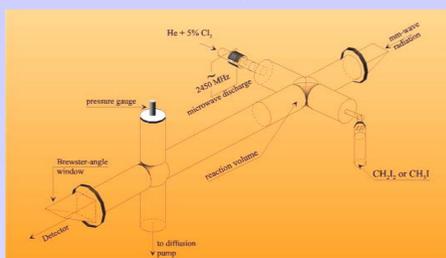$$\chi_{cc}=-(\chi_{aa}+\chi_{bb})=+652\,MHz$$

The Experiments

1. FTMW (Shizuoka University):

➢ Precursors: CH_2I_2 or CH_3I

➢ Backing pressure: 1.5 atm (Ar)

➢ Pulsed discharge: 1.2 kV

ortho CH_2I (even K_a)

$N_{K_aK_c}$ = $1_{01} \leftarrow 0_{00}$
$J\ (= N + S)$ = 3/2 ← 1/2
$F_1\ (= J + I_I)$ = 4 ← 3
$F\ (= F_1 + I_{H_a})$ = 5 ← 4

2. Millimeter-wave (Lab. PhLAM, Lille 1 University):

➢ Precursors: CH_3I or CH_2I_2 reacting with atomic Cl (for H or I abstraction reaction)

➢ Temperature: partial cooling of the absorption cell by limited liquid nitrogen flow

➢ Detected by-products: stable: CH_2ICl (CH_2I + Cl), ICl, CH_3Cl ; transient: CH_2Cl (CH_3Cl + Cl)

hyperfine structure due to iodine (I_I = 5/2) in CH_2I:
$N = 26 \leftarrow 25,\ K_a = 4\ (K_c = N, N+1),\ J = 26\tfrac{1}{2} \leftarrow 25\tfrac{1}{2},\ F_1 = J+I_I$

transition from an unidentifed, non-paramagnetic species

$F_1 = 25 \leftarrow 24$
$F_1 = 26 \leftarrow 25$
$F_1 = 27 \leftarrow 26$
$F_1 = 24 \leftarrow 23$
$F_1 = 28 \leftarrow 27$
$F_1 = 29 \leftarrow 28$

no magnetic field   magnetic field (~150 Gauss)

Observations & Results

➢ Calculations:
✓ predictions & least-squares analysis made with H.M. Pickett's SPFIT & SPCAT
✓ 32 parameters determined (including nuclear spin-rotation constants, not shown)
✓ σ_{fit} = 30 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_a): the G.S. is $^2B_1$, meaning the radical is planar in its ground vibrational state
✓ MMW spectroscopy:
- $12 \leq N' \leq 35$, $K_a' \leq 6$ between 200 – 610 GHz
- hyperfine structure due to iodine nuclear spin partly resolved

Constant /MHz	predicted	determined
A	273120	276676.3(33)
$B+C$	17343	17509.9416(40)
$B-C$	242.0	283.1023(40)
ε_{aa}	–45000	–29409.791(12)
$\varepsilon_{bb}+\varepsilon_{cc}$	–800	–717.720(39)
$\varepsilon_{bb}-\varepsilon_{cc}$	–1200	–1135.306(39)
$a_F^{[I]}$	+16.6	–15.8370(5)
$T_{aa}^{[I]}$	–148	–152.9605(8)
$\tfrac{1}{4}(T_{bb}-T_{cc})^{[I]}$	–93	–107.7451(11)
$\chi_{aa}^{[I]}$	–1740	–1745.0225(34)
$\tfrac{1}{4}(\chi_{bb}-\chi_{cc})^{[I]}$	+109	+108.5243(37)
$a_F^{[H]}$	–60.208	–57.6056(9)
$T_{aa}^{[H]}$	–21.89	–20.712(3)
$\tfrac{1}{4}(T_{bb}-T_{cc})^{[H]}$	+7.02	+4.10(64)

CH_2Br values

Typical values of α-hydrogen in π-radicals:
The unpaired electron is mostly located on the carbon atom

$a_F^{[I]}$ has been accurately determined, with its sign being unambiguously and surprisingly negative ($a_F^{[X]}$ is positive in other CH_2X radicals !)
Interpretation: spin polarization effect:
The sign results from a balance between $\alpha-$ and $\beta-$ spins on the halogen nucleus. The excess amount of $\alpha-$ spin on the s orbital induced by spin polarization systematically decreases from 0.35% in CH_2F, 0.20% in CH_2Cl, to 0.071% in CH_2Br, and –0.038% in CH_2I.

The relationship for π-radicals : $T_{aa}^{[I]} \approx T_{bb}^{[I]} \approx -\tfrac{1}{2}T_{cc}^{[I]}$ is satisfied:
the ground electronic state is $^2B_1$
Unpaired electron density on the p_π orbital of I: 18%
(13.3% in CH2F, 15.7% in CH2Cl, 15.8 in CH2Br)

➢ Conclusion:

CH_2I radical ($^2B_1$ ground state) has been characterized in the gas phase for the first time by high-resolution molecular spectroscopy.

The observed fine 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 CH_2X halogen-substituted radicals.

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