Vibrational Spectra of Chloroform, Freon-11 and Selected Isotopomers in the THz Frequency Region

Christa Haase, Jinjun Liu*, Frédéric Merkt,
Laboratorium für physikalische Chemie, ETH Zürich

*current address: Department of Chemistry, Laser Spectroscopy facility, The Ohio State University.

The Chloroform and Freon-11 Molecules

Freon-11:

CFC compound, high ozone depletion potential, widely used as refrigerant in past

Chloroform:

volatile organic compound, can contribute to the formation of harmful ground-level ozone

Relevant atmospherical compounds.

freon-11

chloroform

Short Review on "THz"

THz region: between 0.1-11 THz (1 THz = 33.36 cm^{-1})

Spectroscopy in THz region challenging because:

i) generation of coherent, narrowband, relatively high-power radiation difficult

ii) sensitive detection difficult

Rotational transitions of light molecules (for example diatomics)

Low-frequency vibrational transitions of molecules and clusters

Overview

Our Method of Generating THz Radiation

Pulsed, widely tunable, narrow-bandwidth, high peak-power source

The $CHCl_3$ and $CFCl_3$ Molecules (and Isotopomers)

The fundamental of the ν_6 mode
Spectra
Analysis

Towards Mass-Selective THz Spectroscopy

High-resolution spectroscopy in a molecular beam

Conclusions

Experimental Configuration

Pulse length:
40 ns (10 ns - 1 μs), Programmable pulse shape

Repetition rate:
25 Hz

Peak power:
~10 -100 μW

Frequency:
tunable between 0.1-11 THz

Bandwidth:
FWHM ~ 10 MHz (Fourier-transform limited)

[1] J. Liu et al., Appl. Phys. Lett. 93 (2008) 131105.

→ **Ideally suited for 1+1' two-photon excitation/ionization experiments under jet-cooled conditions**

Existing Spectra of Asymmetric Deformation Mode

Difficult to find actual IR spectra, although values for transition frequency known (very weak band):

$^{12}CH^{35}Cl_2{}^{37}Cl$: 259.9 cm^{-1} [2]
$^{12}CH^{35}Cl_3$: 261 cm^{-1} [3]
$^{12}CF^{35}Cl_3$: 243 cm^{-1} [4]

Frequencies of different chlorine isotopomers not resolved

Values of certain rovibrational constants not very accurately determined

Raman Spectra of ν_6

Figure 5. The observed and calculated band contours of the *e* species fundamentals of $H^{12}CCl_3$. The instrumental settings were as follows : ν_4, slit widths 150/300/150 μm, gain 200 c/s, tc 2 s ; ν_5, 125/250/125 μm, gain 500 c/s, tc 2 s ; ν_6, 85/200/85 μm, 500 c/s, tc 2 s.

Figure 6. The observed and calculated band contour of the *e* species fundamentals of $H^{13}CCl_3$. The instrumental settings were as follows : ν_4, 200/350/200 μm, gain 500 c/s, tc 1 s ; ν_5, 100/205/100 μm, gain 500 c/s, tc 1 s and ν_6, 100/285/100 μm, gain 1000 c/s, tc 1 s.

[5] R. J. H. Clark et al., Mol. Phys. 31 (1976) 65-81.

[2] A. Ruoff et al., Spectrochim. Acta 26A (1970) 989-997. [3] R. Anttila et al., Mol. Phys. 102 (2004) 1537-1542.
[4] R.J.H. Clark et al., J. Mol. Spectrosc. 56 (1975) 386–398.

The ν_6 vibrational mode of $CHCl_3$, $CFCl_3$ and Isotopomers

Molecule is of C_{3v} symmetry

ν_6 of E symmetry (doubly degenerate)

Fundamental transition frequency of this mode in $^{12}CH^{35}Cl_3$ at 7.82 THz (261 cm^{-1})

Vibrational transition frequencies and vibrational motion of other isotopomers (and $CFCl_3$) similar

Spectra of $CHCl_3$ and Isotopomers

A: Spectra of $^{12}CHCl_3$ and chlorine isotopomers, simulated contours.

B: Spectra of $^{12}CDCl_3$ and chlorine isotopomers.

C: Spectra of $^{13}CHCl_3$ and chlorine isotopomers.

Peaks marked by asterisk* : impurities from other chloroform isotopes.

Pure vibrational transition frequencies determined by simulation.

[5] C. Haase et al., J. Mol. Spectrosc. 262 (2010) 61–63.

Spectra of $CHCl_3$ and Isotopomers

Natural abundance of different chlorine isotopomers:
$^{y}CX^{35}Cl_3$: 43.52%,
$^{y}CX^{37}Cl^{35}Cl_2$: 41.73%,
$^{y}CX^{37}Cl_2{}^{35}Cl$: 13.34%,
$^{y}CX^{37}Cl_3$: 1.42%

Bands for isotopomers of C_s symmetry (^{37}Cl & ^{35}Cl) should split into A' and A" mode, no evidence at this resolution.

Spectra of $^{12}CFCl_3$ and chlorine isotopomers also measured, not shown here.

[5] C. Haase et al., J. Mol. Spectrosc. 262 (2010) 61–63.

Fundamental Transition Frequencies

Values given in units of THz.

[a] Calculated values at MP2/cc-pVTZ level of theory.

[b] Experimental uncertainty is larger for $^{12}CFCl_3$ than for the other molecules because of partial overlap with a water line.

[5] C. Haase et al., J. Mol. Spectrosc. 262 (2010) 61–63.

	Sym.	Expt.	Calc.[a]
$^{12}CHCl_3$			
$^{12}CH^{35}Cl^{37}Cl_2$	a'	7.6725(20)	7.798
	a''		7.822
$^{12}CH^{35}Cl_2{}^{37}Cl$	a''	7.7400(20)	7.869
	a'		7.889
$^{12}CH^{35}Cl_3$	e	7.8076(20)	8.008
	Sym.	Expt.	Calc.[a]
$^{12}CDCl_3$			
$^{12}CD^{35}Cl^{37}Cl_2$	a'	7.6428(20)	7.766
	a''		7.791
$^{12}CD^{35}Cl_2{}^{37}Cl$	a''	7.7096(20)	7.835
	a'		7.857
$^{12}CD^{35}Cl_3$	e	7.7768(20)	7.915
	Sym.	Expt.	Calc.[a]
$^{13}CHCl_3$			
$^{13}CH^{35}Cl^{37}Cl_2$	a'	7.6604(20)	7.783
	a''		7.809
$^{13}CH^{35}Cl_2{}^{37}Cl$	a''	7.7279(20)	7.854
	a'		7.875
$^{13}CH^{35}Cl_3$	e	7.7949(20)	7.933
	Sym.	Expt.[b]	Calc.[a]
$^{12}CFCl_3$			
$^{12}CF^{35}Cl^{37}Cl_2$	a'	7.2058(20)	7.307
	a''		7.345
$^{12}CF^{35}Cl_2{}^{37}Cl$	a''	7.2593(20)	7.364
	a'		7.400
$^{12}CF^{35}Cl_3$	e	7.3140(30)	7.438

Current Work: Ionization - Detected THz Spectroscopy

Supersonic jet expansion

Vibrational excitation followed by photoionization of upper vibrational level (VUV photon)

Tuning of THz source, detection of ions → mass/conformation-selective vibrational spectra

Excitation Scheme

A: VUV generation by four-wave mixing

B: Ionization of molecule/cluster

THz spectroscopy of Rydberg states by pulsed-field ionization possible

skimmer chamber
bolometer
gas nozzle
skimmer
90° off-axis parabolic mirror
VUV detector
electrode stack
VUV beam
UHMW PE windows
90° off-axis parabolic mirror
gas nozzle
grating
MCP detector
THz beam
DAST crystal
main chamber
mono-chromator
THG chamber

Conclusions

A laser-based source of tunable THz radiation has been used to obtain information on low-frequency vibrations of chloroform, freon-11 and several of their isotopomers.

Fundamental transition frequencies of CCl_3 asymmetric deformation mode of these molecules were determined with precision of better than 3 GHz.

Development of experimental configuration that makes it possible to record mass-selective THz spectra in a molecular beam in progress, (close to completion).

Elements of the Energy Matrix

The diagonal elements in the energy matrix are given by:

$$T_6(l,J,K) = \nu_0 + B_6 J(J+1) + (C_6 - B_6)K^2 - D^J J^2(J+1)^2$$
$$- D^{JK} J(J+1)K^2 - D^K K^4 - 2(C\zeta)_6 Kl$$

The off-diagonal elements due to l(2,2) resonance (coupling between $\Delta l = \Delta K = 2$ levels):

$$\langle v_6 = 1, l_6 = -1; J; K-1 | H | v_6 = 1, l_6 = +1; J; K+1 \rangle$$
$$= -1/2\, q_6 [J(J+1) - K(K-1)]^{1/2} [J(J+1) - K(K+1)]^{1/2}$$

The value of $(C_6 - B_6 - C_6 \zeta_6)$ was determined very accurately with microwave spectroscopy. However, C_6 and ζ_6 cannot be determined independently, a calculated value for C_6 is therefore used.

[3] R. Anttila et al., Mol. Phys. 102 (2004) 1537-1542.

frequency stabilization and calibration
Nd:YVO4
Ti:Sa ring laser (fixed)
FR
PBS
AOM
Nd:YVO4
Ti:Sa ring laser (tunable)
FR
PBS
AOM
frequency stabilization
OF
OI
FR
Ti:Sa
Nd:YAG
OI
FR
DAST
OAPM
monochro-mator
PE
PE
THG chamber
pump
Bolometer
Nd:YAG
532 nm
Dye Laser 2
833 nm
355 nm
Dye Laser 1
BBO
250 nm
SFG around 92000 cm-1 using the
Xe 5p5 6p[1/2]0 <= Xe 5p6 resonance
at 80118.974 cm-1

OAPM
bolometer
main
chamber
THz
generation
mono-
chromator
THG
chamber

Outlook

Vibrational Spectroscopy of rare-gas clusters will most likely need development of multipass or other configuration that increases aborption-path length

Possibility of recording spectra of molecules whose torsional motion lies in the THz frequency range (one example: dimethyl ether)...?

Possibility of doing THz spectroscopy on Rydberg states (absorption strength not expected to be a problem)

Advantages of the Planned Experimental Setup

Advantages of working in a molecular beam:

i) Low temperature (less spectral congestion)
ii) No pressure broadening
iii) Easier to measure rare-gas clusters later on

Advantages of detecting ions:

i) background-free
ii) detection of absorption (not transmission)
iii) isotopomer-selective (no need for isotopically pure sample)

Avoid problem of interfering water lines