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

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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 atmospheric compounds.
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 $\nu_6$ 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)

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→ 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):

\[ {^{12}C}H^{35}Cl_2^{37}Cl : 259.9 \text{ cm}^{-1} \] [2]
\[ {^{12}C}H^{35}Cl_3 : 261 \text{ cm}^{-1} \] [3]
\[ {^{12}C}F^{35}Cl_3 : 243 \text{ cm}^{-1} \] [4]

Frequencies of different chlorine isotopomers not resolved

Values of certain rovibrational constants not very accurately determined

The $\nu_6$ vibrational mode of CHCl$_3$, CFCl$_3$ and Isotopomers

Molecule is of $C_{3v}$ symmetry

$\nu_6$ 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
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.

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.

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.

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
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).
The diagonal elements in the energy matrix are given by:

\[ T_6(1, J, K) = \nu_0 + B_6 J(J+1) + (C_6 - B_6) K^2 - D^J J^2 (J+1)^2 \]
\[ - D^K J(J+1) K^2 - D^K K^4 - 2(C\zeta)_6 KL \]

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

\[ \langle \nu_6=1, l_6=-1; J; K-1 | H | \nu_6=1, l_6=+1; J; K+1 \rangle \]
\[ = -1/2 q_6 [ J(J+1) - K(K-1) ]^{1/2} [ J(J+1) - K(K+1) ]^{1/2} \]

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

Nd:YVO₄

Ti:Sa ring laser (fixed)

Nd:YVO₄

Ti:Sa ring laser (tunable)

AOM

FR

PBS

AOM

FR

 PBS

frequency stabilization and calibration

frequency stabilization

Ti:Sa

Nd:YAG

FR

PBS

AOM

FR

PBS

OIF

OF

DAST

OAPM

PE

THG chamber

monochromator

pump

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 5p⁷6p[1/2] ← Xe 5p⁶ resonance at 80118.974 cm⁻¹
OAPM

THz generation

main chamber

mono-chromator

bolometer

THG chamber
Outlook

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