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Vibrational spectra of chloroform, freon-11 and selected isotopomers in the terahertz region

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

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Abstract

The fundamental bands of the CCl_3 asymmetric deformation modes of selected isotopomers of chloroform ($CHCl_3$) and freon-11 ($CFCl_3$) have been measured in a static cell at ambient temperature using a laser-based source of tunable radiation in the terahertz region of the electromagnetic spectrum. The analysis of the rotational contours of the bands enabled the derivation of the fundamental frequencies with an accuracy of better than 3 GHz.

Keywords: THz spectroscopy, vibrational spectrum

Spectroscopy in the terahertz (THz) region of the electromagnetic spectrum (0.1-10 THz) is challenging because the generation and detection of radiation in this region is difficult. Despite recent progress with radiation sources in the THz region, such as backward-wave oscillators (BWO) [1, 2,

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3, 4, 5], photoconductive antennas [6, 7], and quantum-cascade lasers [8], narrowband, widely tunable THz sources are still scarce [9]. Recently, we developed a source of THz radiation [10, 11], which is based on difference-frequency mixing of near-infrared (NIR) radiation in 4-N,N-dimethylamino-4$'$-N'-methyl stilbazolium tosylate (DAST) crystals [10, 12] and is capable of generating narrowband radiation (FWHM $\sim$10 MHz) from 0.1 to 10 THz. This source is particularly suitable for molecular spectroscopy of low-frequency vibrations. This note presents the vibrational spectra of the atmospherically relevant freon-11 (CFCl$_3$), chloroform and selected isotopomers recorded in the region between 7 and 8 THz using this source.

CHCl$_3$ and CFCl$_3$ are prototypical oblate-top molecules with C_{3v} symmetry and have been investigated comprehensively in both experimental and theoretical works. The pure rotational spectra of the vibronic ground state and of the first excited vibrational levels of the degenerate (e) modes ν_5 [13] and ν_6 [14] of chloroform have been measured previously, and so have rotationally resolved infrared spectra of the fundamental bands of the degenerate modes ν_4 [15] and ν_5 [13]. For the lowest vibrational level ν_6, the fundamental transition wavenumber was determined from low-resolution infrared [16] and Raman [17, 18] spectra to be $\sim$260 cm^{-1} (7.80 THz), but none of the infrared

2

and Raman spectroscopic studies [16, 17, 18] reported so far have provided information on the fundamental bands of the different chlorine isotopomers. The situation is very similar for the asymmetric deformation modes of $CFCl_3$ and its isotopomers, for which only Raman spectra recorded at moderate resolution have been reported (see, for instance, Ref. [19]).

We report here a measurement of the absorption spectra of $^{12}CHCl_3$, $^{13}CHCl_3$, $CDCl_3$ and $CFCl_3$ with natural isotopic abundance of chlorine in the region of the ν_6 fundamental band. This mode is of e symmetry for the C_{3v} isotopomers but splits into two modes, $\nu_6(a')$ and $\nu_9(a'')$, in isotopomers of C_s symmetry (we follow the usual convention for numbering the normal modes, see p. 25 of Ref. [20]).

The experimental setup was identical to the one described in Ref. [11] and was placed under an N_2-purged plexiglas cage to reduce water absorption. $^{12}CHCl_3$, $^{13}CHCl_3$, $^{12}CDCl_3$ and $^{12}CFCl_3$ were supplied by Sigma-Aldrich ($\geq 99.5\%$ purity) and used without further purification. A one-meter-long absorption cell with white, ultra-high molecular weight (UHMW) polyethylene windows was filled with 120 mbar ($^{13}CHCl_3$) or 200 mbar (all other compounds) of the sample gas. A 4-Å-mesh molecular sieve was placed in both the liquid sample and the absorption cell to adsorb water and so reduce

3

the interference of water absorption lines. The THz transmission signal was measured using a 4.2 K germanium bolometer and divided by the square of the NIR power for normalization purposes. Because of the width of several GHz of the observed bands (see below), calibrating the NIR radiation frequency with an accuracy of $\sim$1 GHz using a commercial wavemeter turned out to be amply sufficient.

The spectra of $^{12}CHCl_3$, $^{12}CDCl_3$ and $^{13}CHCl_3$ with natural isotopic abundance of chlorine are displayed in Figs. 1a), b) and c), respectively, and reveal the rotational band contours of the fundamental transitions of the CCl_3 asymmetric deformation mode. The relative intensities of the transitions of the different chlorine isotopomers within one spectrum result from the natural abundance of the chlorine isotopes: $^xCY^{35}Cl_3$: $^xCY^{35}Cl_2^{37}Cl$: $^xCY^{35}Cl^{37}Cl_2$ (x=12,13, Y=D,H) = 43.5 : 41.7 : 13.3. The positions of the ν_6 fundamental bands of $^xCY^{37}Cl_3$ coincide with an intense water line, observed on the far left of the spectra depicted in Figs. 1a) and b). Peaks marked by an asterisk correspond to impurities from other chloroform isotopes that were present within the cell and helped to confirm the measured isotopic shifts. Similar spectra of $CFCl_3$ (not shown) with natural abundance of chlorine were also recorded. Decreasing the vapor pressure reduced the

4

pressure broadening without inducing a measurable shift of the band origins. The precision of the measurement was limited by pressure broadening in combination with spectral congestion, which prevented us from resolving individual rotational lines. Under these conditions, the central Q branch represents the spectral feature most suitable to derive the vibrational transition frequencies. The minimum pressure compatible with a satisfactory signal-to-noise ratio is limited to ≈ 50 mbar by the sensitivity of the measurement, which itself is limited by the pulse-to-pulse fluctuations of the laser power (see Ref. [11] for further details). Using a longer (or a multipass) absorption cell would enable a further reduction of the pressure.

A computer program was developed to simulate the frequencies and intensities of the rovibrational transitions of the ν_6 fundamental band of the isotopomers of C_{3v} symmetry. The Hamiltonian used for this simulation is the same as the one given in Eqs. (1-2) of Ref. [15], which includes the Coriolis interaction and the $l(2,2)$ interaction. Rotational contours were generated by convolution with a Lorentzian line profile with a full width at half-maximum of 1 GHz. The program was tested with the available pure rotational and rovibrational spectra reported in Refs. [13] and [14].

The main intensity contribution to the sharpest feature observed in the

5

spectra displayed in Fig. 1 arises from the central Q-branch of the vibrational band because other branches are spread out over a very broad range. In isotopomers of C_s symmetry, the ν_6 mode splits into two modes, ν_6 and ν_9 of A' and A'' symmetry, respectively. Our spectra do not reveal any evidence for this splitting. Firstly, the band maxima of the different chlorine isotopomers shift linearly with increasing number of ^{37}Cl atoms (by $-67.5(3)$ MHz per additional ^{37}Cl atom in ^{12}CHCl$_3$, $-67.0(3)$ MHz in ^{12}CDCl$_3$, $-67.3(3)$ MHz in ^{13}CHCl$_3$ and $-54.1(6)$ MHz in ^{12}CFCl$_3$). Secondly, the shapes of the unresolved Q-branches of all isotopomers appear identical within the resolution and sensitivity limits of the present measurement. The harmonic vibrational frequencies of the $\nu_6(a')$ and $\nu_9(a'')$ modes calculated *ab initio* also appear degenerate within the expected precision limit of the method used (see Table 1).

In simulating the ν_6 fundamental band of ^{12}CH^{35}Cl$_3$, the ground state molecular constants were fixed to the values given in Table 1 of Ref. [15] and those of the vibrationally excited state to those listed in Table VIII of Ref. [14]. In particular, the value of $(C_6 - B_6 - C_6\zeta_6)$ was fixed to -87.23874 MHz as reported in Ref. [14]. Simulations with the same value for $(C_6 - B_6 - C_6\zeta_6)$, but values for ζ_6 of 0.84 (dashed line), 0.86 (full line)

and 0.88 (dotted line) are also shown in Fig. 1. Comparison with the experimental data suggests that the value of 0.86 for ζ_6 proposed in Ref. [14] yields the best agreement.

From the simulations, we conclude that the band maximum is shifted by ~ 0.5 GHz with respect to the vibrational band origin for all compounds investigated. When also considering the uncertainty of the NIR laser frequency (see above) and the uncertainty in the location of the intensity maximum, an overall uncertainty in the band origins of 2 GHz results for all compounds except $CF^{35}Cl_3$, for which an uncertainty in the fundamental frequency of 3 GHz results from the partial overlap of the central Q-branch with a water line. The fundamental transition frequencies are listed in Table 1, where they are compared with values calculated *ab initio* at the MP2/cc-pVTZ level of theory with frozen-core approximation for the CCl_3 asymmetric deformation mode [21]. The calculated harmonic frequencies systematically overestimate the experimental fundamental frequencies by a factor of ~ 1.02.

In summary, 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. In future, we plan to use the same radiation source to measure THz spectra of molecules in supersonic jet expansions to

partially resolve their rotational structure. In the experiment, the vibrational excitation will be followed by photoionization of the upper vibrational level using another laser source. By tuning the frequency of the THz source and detecting the photoions, this double-resonance scheme should enable sensitive, background-free and isotopomer-selective absorption measurements.

Acknowledgments

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^{12}CHCl$_3$			
	sym.	expt.	calc.[a]
^{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
^{12}CDCl$_3$			
	sym.	expt.	calc.[a]
^{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
^{13}CHCl$_3$			
	sym.	expt.	calc.[a]
^{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
^{12}CFCl$_3$			
	sym.	expt.[b]	calc.[a]
^{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

Table 1: Experimental and calculated fundamental frequencies of the CCl$_3$ asymmetric deformation modes of chloroform, freon-11 and selected isotopomers in units of THz. This mode corresponds to ν_6 for molecules of C_{3v} symmetry and ν_6 and ν_9 with A' and A'' symmetry, respectively, for molecules of C_s symmetry. The numbers in parentheses represent the experimental uncertainties. a): Calculated values at MP2/cc-pVTZ level of theory with frozen-core approximation, unscaled. b): The experimental uncertainty is larger for ^{12}CF^{35}Cl$_3$ than for the other molecules because of the partial overlap of the central Q-branch with a water line (see text for details).
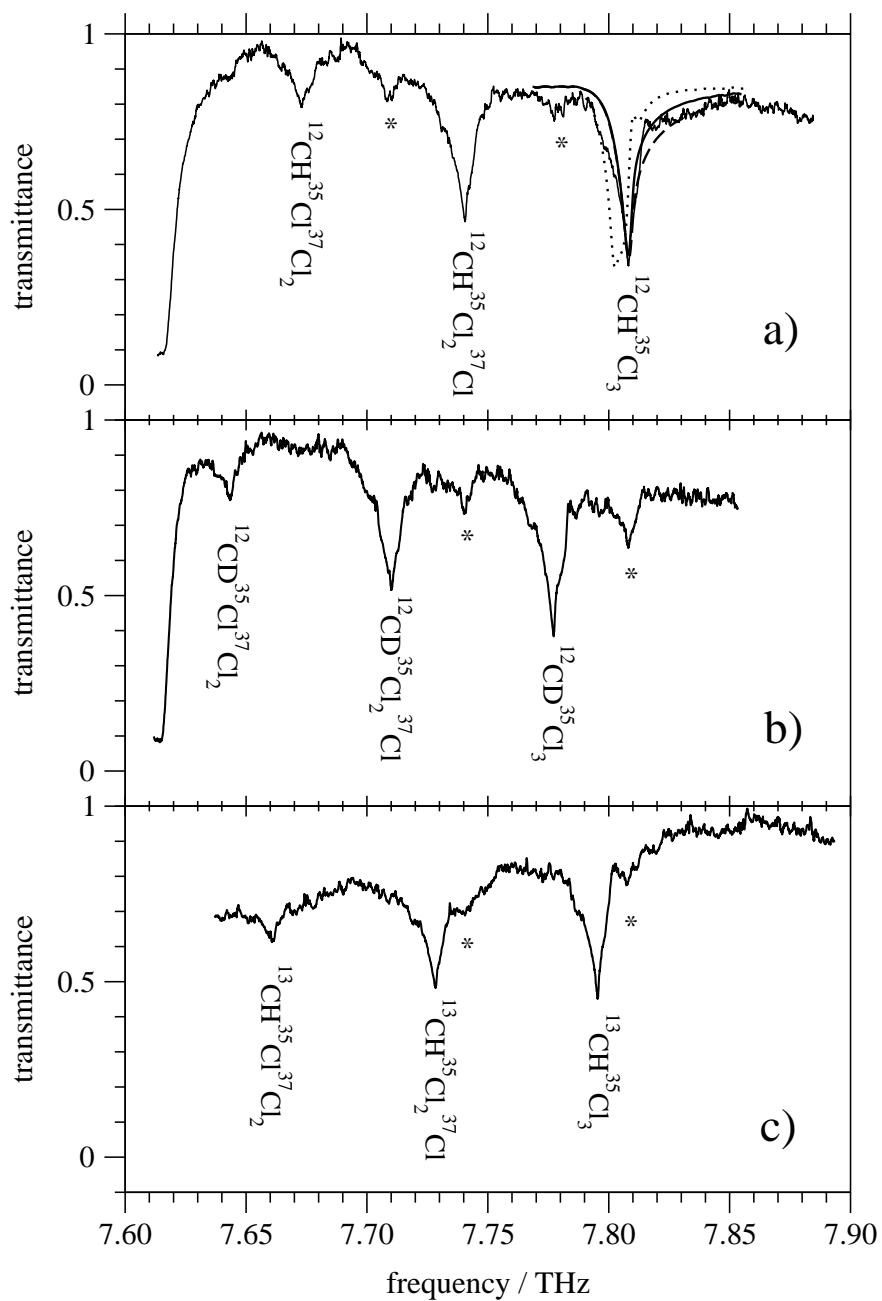
Figure 1: Spectra of the fundamental band of the CCl_3 asymmetric deformation mode of chloroform and selected isotopomers. The strong line on the far left-hand side of the spectra in a) and b) corresponds to a water line. The lines marked by asterisks correspond to impurities of $^{12}CDCl_3$ in panel a) and $^{12}CHCl_3$ in panels b) and c). In panel a), simulated profiles of the $^{12}CH^{35}Cl_3$ isotopomer, assuming values of 0.84 (dashed line), 0.86 (full line) and 0.88 (dotted line) for ζ_6 are displayed (see text for details).