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CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4: Infrared spectra, radiative efficiencies, and global warming potentials

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ABSTRACT

Infrared spectra for the title compounds were measured experimentally in 700 Torr of air at 295 K and systematically modeled in B3LYP, M06-2X and MP2 calculations employing various basis sets. Calibrated infrared spectra over the wavenumber range 600–3500 cm^{-1} are reported and combined with literature data to provide spectra for use in experimental studies and radiative transfer calculations. Integrated absorption cross sections are (units of cm^{-1} $molecule^{-1}$): CH_3Cl, 660–780 cm^{-1}, $(3.89 \pm 0.19) \times 10^{-18}$; CH_2Cl_2, 650–800 cm^{-1}, $(2.16 \pm 0.11) \times 10^{-17}$; $CHCl_3$, 720–810 cm^{-1}, $(4.08 \pm 0.20) \times 10^{-17}$; and CCl_4, 730–825 cm^{-1}, $(6.30 \pm 0.31) \times 10^{-17}$. CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 have radiative efficiencies of 0.004, 0.028, 0.070, and 0.174 W m^{-2} ppb^{-1} and global warming potentials (100 year horizon) of 5, 8, 15, and 1775, respectively. Quantum chemistry calculations generally predict larger band intensities than the experimental values. The best agreement with experiments is obtained in MP2(Full) calculations employing basis sets of at least triple-zeta quality augmented by diffuse functions. The B3LYP functional is found ill-suited for calculating vibrational frequencies and infrared intensities of halocarbons.

1. Introduction

Chloroalkanes are of interest in atmospheric chemistry because of their ability to contribute to chlorine-catalyzed stratospheric ozone loss and to radiative forcing of climate change. Quantitative infrared absorption spectra are required to evaluate the contribution of chloroalkanes to radiative forcing of climate change. In our recent review of the radiative efficiencies and global warming potentials of halocarbons we noted inconsistencies in the literature database for quantitative infrared absorption spectra of the chloromethanes [1]. For example there are approximately 20–30% discrepancies in the intensities of the published spectra for $CHCl_3$ and CCl_4. To improve the database of IR spectra of halocarbons for assessments of radiative forcing of climate change we present new results of an experimental and computational study of the IR spectra of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. We provide a critical comparison of our results with the spectra available in the literature and from online databases and present spectra recommended for use in radiative transfer calculations.

Numerous theoretical calculations of infrared absorption cross sections for estimation of global warming potentials (GWP) exist in the literature [1]. In many of

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these studies the choice of quantum chemistry level of theory and basis set size is dictated by routine or by limited computational resources; examples of the commonly employed methods include B3LYP/6-31G* [2–5], B3LYP/6-31G** [6,7], B3LYP/6-311G** [8], and MP2/6-31G** [5]. Systematic studies show that the abovementioned methods are far from optimal. Jensen [9–12] has benchmarked basis sets suitable for systematically approaching the basis set limit for Hartree-Fock and density functional methods. In short, Jensen's systematic studies show that basis sets of at least triple-zeta quality augmented by diffuse functions are necessary to ensure that the calculated structures, harmonic vibrational frequencies and infrared intensities are reasonably close to the basis set limit results. Galabov et al. [13] investigated various correlated levels of theory (MP2, CISD, CCD, QCISD, CCSD and CCSD(T)) and arrived at the same conclusion: at least triple-zeta basis sets augmented by diffuse functions are needed to "produce plausible accord between theory and experiment".

The present work has three goals: (i) to present the results from a comprehensive experimental and computational study of the IR spectra of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4; (ii) to compare these results with the available literature data and provide recommended spectra for use in radiative transfer calculations and experimental studies; (iii) to provide radiative efficiency and global warming potentials for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

2. Methods

2.1. Experimental details

The apparatus used to measure the spectra has been described previously (Wallington and Japar [14], Pinnock et al. [15]). The apparatus consists of a Mattson Instruments Sirius Fourier transform infrared spectrometer coupled to a 140 l, 2 m long, evacuable Pyrex chamber and a narrow band MCT detector. Internal White type multiple reflection optics provide a path length of 27.4 m. The spectrometer was operated at a spectral resolution of 0.25 cm^{-1} over the spectral range of 650–3500 cm^{-1}. Frequency calibration was achieved using the interferometer laser with an uncertainty of ± 0.09 cm^{-1}. Samples of the chloromethanes were obtained from commercial sources at stated purities $>99.9\%$ and were subjected to repeated freeze-pump-thaw cycling to remove volatile impurities. Mixtures of the chloromethanes were made up with 700 Torr of air at 295 K and introduced into the chamber and their concentrations were adjusted such that the absorption features were unsaturated.

2.2. Computation details

Frozen core MP2 [16] and DFT calculations employing the M06-2X [17], Becke 3 parameter [18], and Lee-Yang-Parr [19] B3LYP hybrid functionals were carried out with the Gaussian 09 program [20]. Calculations were carried out employing the frequently used 6-31G* basis set and Dunning's correlation-consistent aug-cc-pV*X*Z (*X*=D, T, Q, 5) basis sets [21,22].

Vibrational wavenumbers and infrared intensities, obtained in the harmonic approximation for the title compounds, are provided in Tables S1–S4 in the supplementary information. Results from B3LYP, M06-2X and MP2 calculations on the fluorinated analogs (CH_3F, CH_2F_2, CHF_3 and CF_4) employing the 6-31G* and aug-cc-pVTZ basis sets are provided in Tables S5–S8 in the supplementary information. Additional anharmonic calculations were carried out employing the aug-cc-pVTZ basis set.

3. Results

3.1. 1 Experimental results

As shown in Fig. 1 the absorption features for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 scaled linearly with the sample concentrations in the chamber. The linearity of the plots in Fig. 1 indicates that saturation was not a problem in the present work. Absorption spectra for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 over the range 650–2000 and 650–850 cm^{-1} are displayed in Figs. 2 and 3, respectively. Uncertainties in the spectra are estimated to arise from the following sources: sample concentration, $\pm 2\%$; path length calibration $\pm 1.5\%$; spectrometer accuracy, $\pm 1\%$; residual baseline offset after subtraction of background, $\pm 0.5\%$; and spectrum noise, $\pm 10^{-20}$ cm^2 $molecule^{-1}$ (Pinnock et al. [15]). The total uncertainty in the measured absorption cross sections is estimated to be $\pm 5\%$.

Integrated absorption cross sections measured in the present and previous studies are given in Tables 1–4. The uncertainties listed in Tables 1–4 for the absorption bands measured experimentally in the present work are $\pm 5\%$; those for previous work are as reported in the literature. As seen from Table 1, with the exception of data from Brown et al. [23] there is good agreement in the integrated absorption cross sections reported for CH_3Cl from the

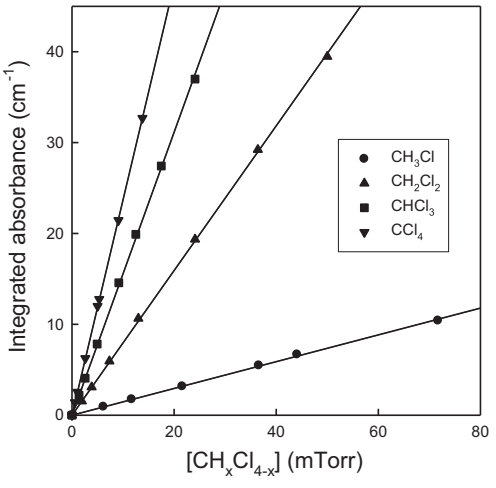

Fig. 1. Plots of integrated absorbance versus CH_xCl_{4-x} concentration: CH_3Cl, circles, 660–780 cm^{-1}; CH_2Cl_2, triangles, 660–800 cm^{-1}; $CHCl_3$, squares, 725–810 cm^{-1}; CCl_4, inverted triangles, 730–825 cm^{-1}.