

Vibrational C–H overtone spectroscopy and bond distances of butenes dissolved in liquid Xe

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ABSTRACT

Vibrational overtone spectra of isobutene, cis-2-butene, and trans-2-butene dissolved in liquid xenon at 163 K, have been recorded between 5000 and 16500 cm^{-1} . Spectral regions for the first four overtones were measured using a Fourier transform spectrophotometer. The fifth overtone ($\Delta\nu = 6$) spectra were recorded with a double beam (pump–probe) thermal lens technique. Band deconvolution allowed isolation of individual transitions. Local-mode parameters were calculated for C–H oscillators in solution and compared with gas phase local-mode parameters. Density functional theory calculations were done to obtain C–H bond lengths and vibrational frequencies for the three butene isomers. Frequency shifts ($\Delta\omega$) with respect to gas phase results are attributed to changes in harmonic frequency and anharmonicity of the particular C–H bond of the sample dissolved in the inert liquid solvent.

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1. Introduction

The C–H overtone spectra of cis-2-butene and trans-2-butene in the gas phase have been reported by Turnbull et al. [1]. They reported transitions with $\Delta\nu = 1$ –9 and calculated oscillator strengths with a harmonically coupled anharmonic oscillator local model and ab initio dipole moment functions. Manzanares et al. [2] obtained the gas phase transitions with $\Delta\nu = 1$ –6 and reported C–H isolated fundamental frequencies and C–H bond lengths estimated from correlation equations. Wong and Moore [3] presented the $\Delta\nu = 6$ transitions and reported correlation equations between $\Delta\nu = 6$ transitions and C–H isolated frequencies and bond lengths measured by McKean and co-workers [4,5].

Thermal lensing experiments with liquefied gases have reported sensitive measurements of the C–H ($\Delta\nu = 6$) overtone of unsaturated hydrocarbons solutions [6–9]. Patel et al. [10–13] used photo-acoustic detection to measure high energy overtones ($\Delta\nu = 4$ –6) of liquid methane, ethylene, and solid para-hydrogen. Manzanares et al. [14–19] continued the photo-acoustic work applied to cryogenic solutions. Thermal lensing studies of vibrational overtone spectroscopy of liquids were originally made by Swofford and co-workers [20,21].

Cryogenic liquid solvents are ideal to study molecules in solution because of the relatively small solute–solvent interactions [22]. For hydrocarbons dissolved in liquefied rare gases, the solvent

does not change the overall shape of the absorption band with respect to the gas phase absorption. The only spectral change corresponds to a shift in the absorption wavenumber and an overall increase in the width of the band [7]. Solvent influence on the absorption of a solute is usually treated with models that take into account the relative permittivity of the solvent, the dipole moment of the molecule under study and the volume of the molecule [23]. Other models take into account the solvent induced changes in the potential energy curve of the bond under study [24–26]. The main reason for this work is to investigate what factors are important to determine the spectral changes and which theoretical models could be successful predicting the changes.

In order to find the harmonic frequency and anharmonicity of a vibration, a series of overtone transitions have to be obtained. The solutions have to be diluted in order to see the influence of the solvent. The solubility of most hydrocarbons in cryogenic solvents is usually in the range 10^{-3} – 10^{-6} mole fraction. Studies of high vibrational levels in cryogenic solutions are scarce because of the technical problems associated with the observation of very weak absorptions with the added difficulty of the low solubility in cryogenic solutions. These studies are now possible because we can obtain absorption bands of vibrational fundamental and overtone levels of the solute in very dilute solutions. We have shown that the thermal lens technique has the sensitivity required to obtain absorption bands of high overtone levels of the solute in very dilute solutions. In particular, a limit of detection has been calculated with measurements of the fifth overtone absorption of methane in liquid nitrogen for solutions of concentration (mole fraction)

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from 3.6×10^{-3} to 1.2×10^{-4} . Calculated limits of detection are 54 and 15 ppm according to two different definitions of limit of detection for the thermal lens technique [6].

In this paper the vibrational overtone spectra of isobutene, cis-2-butene, and trans-2-butene dissolved in liquid xenon at 163 K were recorded between 5000 and 16500 cm^{-1} . The first four overtones were measured using a Fourier transform spectrophotometer and the fifth overtone ($\Delta\nu = 6$) spectra were recorded with a double beam (pump-probe) thermal lens technique. Local-mode parameters were calculated for C–H oscillators in solution and compared with gas phase local-mode parameters.

2. Experimental

The thermal lens effect can be described as a change in refractive index of a liquid induced by absorption of a pump laser. Strong sample heating occurs at the center of the beam where the intensity is greatest, resulting in a lens-like optical element due to the temperature gradient between the beam center and the bulk. In most materials a temperature increment lowers the refractive index. The thermo-optical element is shaped as a negative lens that causes the laser beam to diverge. Increased divergence may be observed beyond the sample as a larger spot size or lower beam intensity at the center [27,28].

The experimental set up has been described previously [7,8]. In our dual-beam experiment the pump (cw, dye) and probe (cw, Ar ion) lasers are combined collinearly at the surface of a dichroic filter; the beams are then focused before passing through the sample cell. After passing the sample cell, suitable filters isolate the probe beam for detection, which can be carried out with a photomultiplier. The probe intensity, modulated by the fluctuating strength of the thermal lens, is monitored by a lock-in amplifier synchronized to the chopping frequency. Thermal lens signals are also normalized by the output power of the excitation laser transmitted through the beam splitter. Xenon (99.999%) was obtained from Advanced Specialty Gases, while isobutene (99.0%), cis-2-butene (99%) and trans-2-butene (99%) were purchased from Aldrich chemicals. Two laser dyes: Kiton Red covering from 15235 to 16510 cm^{-1} and Rhodamine 6G covering from 15846 to 16956 cm^{-1} were used to scan the $\Delta\nu = 6$ absorption bands.

3. Results

All butene isomers have three non-equivalents CH oscillators which are labeled as CH_o , CH_{ip} , and CH_{op} to refer to the olefinic CH bonds and methyl oscillators in-plane and out-of-plane of the C–C=C bonds, respectively. Fig. 1 shows the non-equivalent C–H bonds of the three isomers. The separate C–H overtone spectra corresponding to isobutene are shown in Figs. 2 and 3. The C–H ($\Delta\nu = 3$ –5) absorption spectra were taken for a solution of isobutene (1.1%) in liquid xenon at 163 K. The deconvoluted C–H ($\Delta\nu = 6$) TLS spectrum was taken for a solution of isobutene (0.15%) in liquid xenon at 163 K. The excitation power of the laser was 125 mW.

The deconvoluted C–H ($\Delta\nu = 3$ –6) spectra of cis-2-butene are shown in Figs. 4 and 5. The FT-NIR spectra were taken for a 1.4 % solution of cis-2-butene in liquid xenon at 162 K. The TLS spectrum was for a 0.10% solution of cis-2-butene in liquid xenon at 163 K with a laser excitation power of 180 mW. The overtone spectra of trans-2-butene dissolved in liquid xenon are shown in Figs. 6 and 7. For the FT-NIR spectra, condensation of the gas mixture was carried out at 163 K, and its molar concentration was 2.7%. The thermal lens spectrum was taken for a trans-2-butene solution

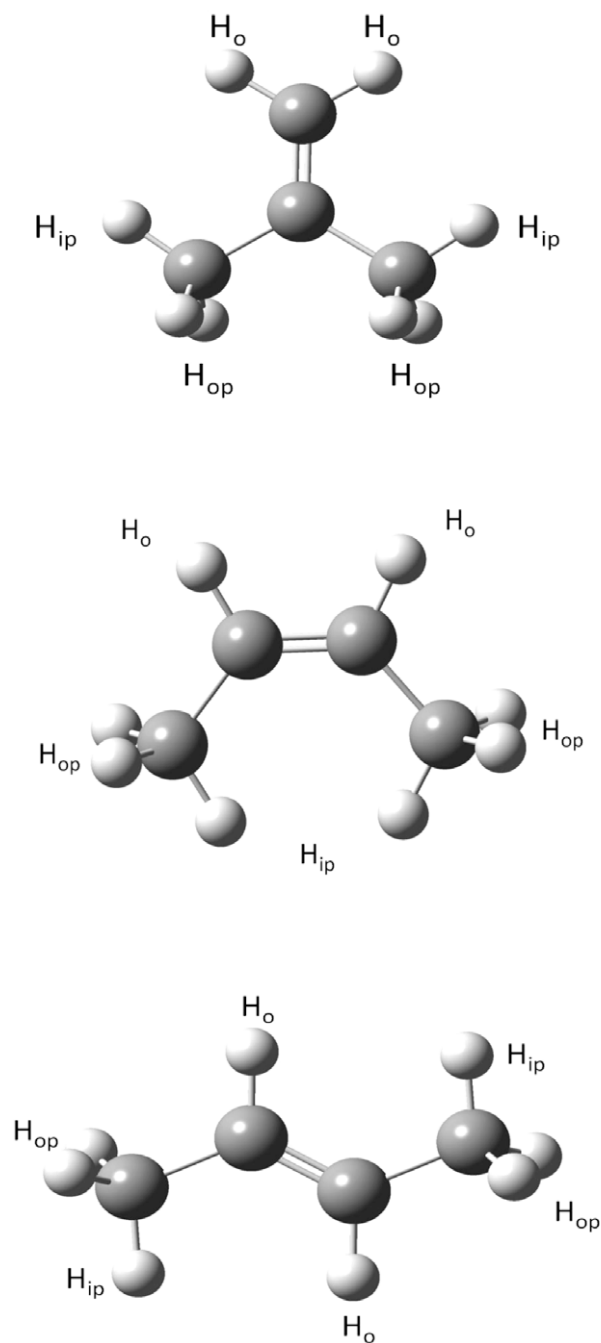


Fig. 1. The optimized geometry of isobutene, cis-2-butene, and trans-2-butene at the DFT level using diffuse basis set functions.

(0.20%) in liquid Xe at 163 K. The laser excitation power was 140 mW, and the chopping frequency 0.50 Hz.

4. Discussion

4.1. Transition frequencies and C–H assignments

For the butene isomers, the energy order of the three oscillators is $\text{CH}_{op} < \text{CH}_{ip} < \text{CH}_o$. Once again, the orientation of the out-of-plane methyl bonds favors anisotropic interaction with π electrons in the double bond, decreasing their vibrational frequency [29]. Frequencies and bandwidths ($\Delta\omega_{1/2}$) for the C–H overtones of isobutene, cis-2-butene and trans-2-butene are summarized in Tables 1–3,

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