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Optical constants, dielectric constants, molar absorption coefficients, molar polarizability, vibrational assignment and transition moments of liquid iodobenzene between 4000 and 400 cm^{-1} at 25 °C

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Abstract

This paper reports the complex refractive index, molar absorption coefficient and imaginary molar polarizability spectra of liquid iodobenzene at 25 °C. The imaginary molar polarizability spectrum was fitted with 184 classical damped harmonic bands to determine the integrated intensity of the individual transitions. The standard deviation of the fitted spectrum from the experimental spectrum is 0.024 cm^3 mol^{-1}, and the R^2 value of the fit is 0.9968 indicating that the fitted spectrum is an accurate representation of the experimental spectrum. The dipole moment derivatives with respect to the normal coordinates and transition moments were determined for 26 of the 30 fundamentals. The total intensities of the in-plane and out-of-plane fundamentals were compared to benzene and other monosubstituted benzene derivatives using the F-sum rule. It was found that the total intensity of the out-of-plane fundamentals is essentially the same for the different compounds while the total intensities for the in-plane fundamentals varies according to the electronegativities of the substituents.
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1. Introduction

In previous papers [1–11] from this laboratory, the optical constants (real and imaginary refractive indices) were reported at 25 °C for liquid bromobenzene, bromobenzene-d_5, hexafluorobenzene, ethylbenzene, toluene-d_8, and fluorobenzene. In addition, the optical constants were determined and published [12–20] for benzene, benzene-d_6, benzene-d, toluene, and chlorobenzene.

A comparison [21] of the integrated intensities of the infrared active fundamentals of benzene and benzene-d_6 revealed noticeable variations between the liquid- and gas-phase for each isotopomer as well as between isotopomers in both phases. This prompted a more detailed analysis [22,23] of the intensities with the determination of the liquid- and gas-phase force field and dipole moment derivatives with respect to symmetry and internal coordinates. It was revealed that the magnitudes of the dipole moment with respect to the CC stretch, HCC bend and HCCC

out-of-plane bend are the same within experimental error in both the liquid- and gas-phases. However, the magnitude of the dipole moment derivative with respect to the CH stretch internal coordinate in the liquid is only about three quarters of the gas-phase value. It was hypothesized that this was due to an interaction, called a pseudo-hydrogen bond, between the H and the electron density of the surrounding π-cloud of the neighbouring molecules. To explore this interaction, this laboratory has been working on determining the integrated intensities in substituted benzenes. The premise of this study is that altering the electron density of the π-cloud will alter the pseudo-hydrogen bond and the resulting magnitudes of the dipole moment derivatives with respect to the CH stretch in the liquid-phase.

This paper continues this study and reports the measurements of the optical constant spectra of iodobenzene. The optical constants were obtained from transmission measurements across the mid-infrared. Methods for calculating optical constants of liquids from the transmission measurements are discussed in detail in the literature [19,24–29].

Due to large variations in absorption across the mid-infrared, the spectrum was divided into smaller regions of similar absorption. The imaginary refractive indices, $k(\tilde{v})$, were determined

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separately for each region from spectra measured in cells with the appropriate pathlengths. These k spectra were then averaged and the average k spectra for each region were merged to create a complete k spectrum across the mid-infrared. The real refractive index spectrum was determined by Kramers–Kronig (KK) transformation of $k(\tilde{v})$ along with n_{el}, the contribution of the electric transitions to the infrared real refractive index [18,25].

Vibrational assignment and dipole moment derivatives with respect to normal coordinates were obtained by curvefitting the imaginary molar polarizability spectrum [13,26].

Equations given in the literature [26] allow other properties of the liquid, including the molar (decadic) absorption coefficient spectrum, $E_m(\tilde{v})$, the complex dielectric constant spectrum, $\hat{\varepsilon}(\tilde{v})$, and the imaginary molar polarizability spectrum, $\alpha''_m(\tilde{v})$, to be calculated from the optical constants. The imaginary molar polarizability is the quantity of choice for studying absolute infrared absorption on a molecular level [19,26].

2. Experimental

The iodobenzene used was purchased from Aldrich and was labeled to be 98% pure. The iodobenzene was used as purchased without any further purification, except samples were kept over molecular sieve to ensure they were free from water.

Experimental spectra were recorded on Nicolet Impact 410 and Thermo-Electron Nicolet 6700 FTIR spectrometers with Ever-Glo mid-IR sources, Ge-on-KBr beamsplitters, and DTGS detectors. Sample and background spectra were recorded at a nominal resolution of 1 cm^{-1} and Happ-Genzel apodization was applied before Fourier transformation.

Experimental absorbance spectra of iodobenzene, and the calibration standard [30], benzene, were measured in fixed-pathlength (FP), variable-pathlength (VP) cells, and temporary cells. The fixed-pathlength cells had KBr, NaCl, or CaF$_2$ windows. The variable pathlength cell and temporary cell had NaCl or KBr windows. Five hundred and twelve interferograms were averaged before Fourier transformation when using VP or FP cells. Two hundred interferograms were averaged before Fourier transformation when a temporary cell was used. A single beam background spectrum was collected before each single beam sample spectrum was recorded.

The pathlengths of most of the FP cells were determined from the fringe patterns in the experimental absorbance spectra of the empty cells using the program PATHLEN [29]. Since the absorbance spectra of the empty 115, 1200, and 1500 μm FP cells did not produce a fringe pattern, the cells had to be calibrated using benzene. Spectra of benzene were measured using the same experimental parameters as the iodobenzene. The spectra were then input to the program IRYTRUE [30–32] which compares the experimental measurements with the accepted standards and determines the cell constant. For cells that displayed a fringe pattern, the cell constants obtained from IRY-TRUE and the cell pathlengths obtained from the fringe patterns agreed within their respective standard deviations.

The experimental absorbance spectra of the empty VP cells did not show a fringe pattern and, therefore, had to be calibrated with benzene. The VP cells were calibrated with micrometer settings ranging from 400 to 750 μm. Since very few of the benzene bands are suitable for calibrations greater than 750 μm, the pathlengths of the cells larger than 750 μm were found by assuming that the calibration of the cells below 750 μm were valid for these pathlengths.

Temporary cells were used to measure regions of the experimental absorbance spectrum where very small pathlengths are required. The average pathlength–area ratio was determined from 3190 to 2945 cm^{-1} for experimental absorbance spectra in a 15, 30, and 50 μm cell. The average ratio and the area of the experimental absorbance spectra in the temporary cell between the same limits were used to calculate the pathlength of the temporary cell.

To aid in the assignment of the fundamentals, *ab initio* calculations were performed with Gaussian 03 Rev B.05 [33] at the HF [34–36] and the MP2 [37–41] levels of theory. Geometry optimization and frequency calculations were completed for the following basis sets: STO-3G [42,43], STO-3G*, 3-21G [44–49], 3-21G*, 3-21G**, CEP-4G [50–52], CEP31G [50–52], CEP121G [50–52], Midi! [53], DZDGP [54,55] and UGBS [56–64] at the HF level and STO-3G, STO-3G*, 3-21G, 3-21G* at the MP2 level.

3. Results and discussion

Table 1 shows the linear absorption coefficients, $k(\tilde{v})$, used to correct the baseline, the real refractive indices at the high wavenumber limit of the region, the pathlength range used, the number of spectra processed for each anchor point, the 95% confidence limit and the uncertainty in $k(\tilde{v})$. When calculating linear absorption coefficients it is important to choose experimental absorbance spectra which have absorbances between, approximately, 0.2 and 2 whenever possible. ANCHORPT [29] requires the real refractive index spectrum to calculate the apparent absorbance due to reflection losses. Performing Kramers–Kronig (KK) transformation on an approximate imaginary refractive index spectrum, of pathlength ∼5 μm, an approximate real refractive index spectrum is obtained which can be used by ANCHORPT. The KK transform also needs the real refractive index value at the high wavenumber limit of the spectrum, 4000 cm^{-1}. To obtain this value, literature values of $n(\tilde{v})$ from the visible region at 25 °C are fit to the equation:

$$n_{el}^2 = a_4\tilde{v}^4 + a_2\tilde{v}^2 + a_0 \tag{1}$$

The coefficients obtained from the fit of the literature data [65] for iodobenzene are $a_4 = 1.97(16) \times 10^{-19}$ cm^4, $a_2 = 2.94(11) \times 10^{-10}$ cm^2, and $a_0 = 2.5141(21)$, where the values in parentheses are the standard deviations in the terminal digits of the parameters. The experimental and fitted data is presented in Fig. 1.

Table 2 shows the regions into which the experimental spectra were divided, the number of spectra processed and the pathlengths used in each region. This table also reports the refractive index at the high wavenumber end of each region, n_H, which were obtained from the approximate n spectrum described above.