Infrared optical constants, dielectric constants, molar polarizabilities, transition moments, dipole moment derivatives and Raman spectrum of liquid cyclohexane

C. Dale Keefe*, Janet E. Pickup

Department of Chemistry, Cape Breton University, 1250 Grand Lake Rd, Sydney, Nova Scotia, Canada B1Y 6L2

ARTICLE INFO

ABSTRACT

Previous studies have been done in this laboratory focusing on the optical properties of several liquid aromatic and aliphatic hydrocarbons in the infrared. The current study reports the infrared and absorption Raman spectra of liquid cyclohexane. Infrared spectra were recorded at 25 °C over a wavenumber range of 7400–490 cm^{-1}. Infrared measurements were taken using transmission cells with pathlengths ranging from 3 to 5000 μm. Raman spectra were recorded between 3700 and 100 cm^{-1} at 25 °C using a 180° reflection geometry. *Ab initio* calculations of the vibrational wavenumbers at the B3LYP/6311G level of theory were performed and used to help assign the observed IR and Raman spectra. Extensive assignments of the fundamentals and binary combinations observed in the infrared imaginary molar polarizability spectrum are reported. The imaginary molar polarizability spectrum was curve fitted to separate the intensity from the various transitions and used to determine the transition moments and magnitudes of the derivatives of the dipole moment with respect to the normal coordinates for the fundamentals.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Previous papers [1,2] reported the infrared optical constant, dielectric constant and imaginary molar polarizability spectra of liquid hexane from transmission measurements. The integrated intensities were determined [2] by curve fitting the imaginary molar polarizability (IP) spectrum. In continuation of our study we report the optical constant, dielectric constant and IP spectra of liquid cyclohexane for the first time. The vibrational wavenumbers of the fundamentals, first overtones and binary combinations are assigned from the infrared and Raman spectra with the aid of density functional theory (DFT) calculations. The integrated intensities of the fundamentals are determined by curve fitting the IP spectrum.

The experimental methods used to obtain the optical constants from the transmission measurements are identical to those used for the previous studies from this laboratory. The methods have been explained in detail in literatures [3–6] and will not be discussed here. All of the computer programs used to determine the optical constants have also been previously reported [7].

2. Experimental

The cyclohexane was obtained from Fisher Scientific as certified ACS grade and was labeled as 99.9% pure. The cyclohexane was used without further purification, and samples were kept over molecular sieve to ensure that they were free of water.

The infrared transmission spectra were measured in fixed pathlength cells (FPC) with pathlengths between 15 and 1500 μm, variable pathlength cells (VPC) with pathlengths between 2000 and 5000 μm and temporary sandwich cells (TSC) with pathlengths between 3 and 4 μm. The pathlengths of the FPC were determined either from the empty cell fringe patterns or by calibration [8,9] with benzene for those that did not give fringe patterns. The pathlengths of the VPC were determined by calibrating (with benzene) the micrometer reading below 750 μm and assuming this calibration held above 750 μm as reported earlier [1]. The pathlengths of the TSC were determined by internal calibration using the absorption between 1485 and 1405 cm^{-1}, which was measured accurately with FPC. Mid-IR measurements were made on both a Nicolet Impact 410 (4000–490 cm^{-1}) spectrometer and a Thermo-Electron Nicolet 6700 (7400–490 cm^{-1}) FTIR spectrometer. Both spectrometers have globar sources, KBr beamsplitters and DTGS detectors. All spectra measured in the FPC and VPC were recorded at 1 cm^{-1} resolution and 512 scans were averaged before FT. The spectra mea-

---

* Corresponding author. Tel.: +1 902 563 1185; fax: +1 902 563 1880.
  E-mail address: Dale_Keefe@CBU.ca (C.D. Keefe).

Table 1
Calculated and experimental fundamental transitions of cyclohexane.

Vibration	Symmetry	Activity	Calculated $\tilde{\nu}$ (cm^{-1})[a]	Scaled calculated $\tilde{\nu}$ (cm^{-1})[b]	Calculated intensity[c]	Experimental $\tilde{\nu}$ (cm^{-1})
ν_1	A$_{1g}$	Raman	3048	2930	405	2937
ν_2	A$_{1g}$	Raman	2988	2873	439	2852
ν_3	A$_{1g}$	Raman	1541	1482	1	1465
ν_4	A$_{1g}$	Raman	1201	1155	0.5	1157
ν_5	A$_{1g}$	Raman	800	769	22	801
ν_6	A$_{1g}$	Raman	374	360	0.5	384
ν_7	A$_{2g}$	Inactive	1101	1059		1059[e]
ν_8	A$_{2g}$	Inactive	1391	1337		1335[e]
ν_9	A$_{1u}$	Inactive	1381	1328		1329[e]
ν_{10}	A$_{1u}$	Inactive	1152	1108		1112[e]
ν_{11}	A$_{1u}$	Inactive	1098	1055		1049[e]
ν_{12}	A$_{2u}$	IR	3054	2936	179	2931
ν_{13}	A$_{2u}$	IR	2994	2879	85	2852[d]
ν_{14}	A$_{2u}$	IR	1537	1477	17	1451
ν_{15}	A$_{2u}$	IR	1056	1015	3	1038
ν_{16}	A$_{2u}$	IR	530	510	0.7	524
ν_{17}	E$_g$	Raman	3043	2925	290	2923
ν_{18}	E$_g$	Raman	2992	2876	86	2870
ν_{19}	E$_g$	Raman	1525	1466	58	1443
ν_{20}	E$_g$	Raman	1387	1334	20	1346
ν_{21}	E$_g$	Raman	1306	1255	44	1266
ν_{22}	E$_g$	Raman	1050	1010	24	1027
ν_{23}	E$_g$	Raman	803	772	1	801
ν_{24}	E$_g$	Raman	433	417	2	425
ν_{25}	E$_u$	IR	3040	2923	290	2924
ν_{26}	E$_u$	IR	2986	2871	57	2852[d]
ν_{27}	E$_u$	IR	1524	1465	16	1448
ν_{28}	E$_u$	IR	1408	1354	0.4	1351
ν_{29}	E$_u$	IR	1310	1259	3	1257
ν_{30}	E$_u$	IR	935	899	5	904
ν_{31}	E$_u$	IR	863	830	4	862
ν_{32}	E$_u$	IR	225	217	0.01	217[e]

[a] Calculated at B3LYP/6-311G level.

[b] Scaling factor of 0.9614, see text for details.

[c] The calculated IR intensities are $A_{j,\text{gas}}$ in km mol^{-1} and the Raman scattering activities are in Å^4 u^{-1}.

[d] Only one band is observed in the experimental spectrum.

[e] Calculated from the assignment of active combinations, see text for details.

sured in the TSC were recorded at 2 cm^{-1} resolution and 200 scans were averaged before FT.

Non-polarized Raman spectra between 3700 and 100 cm^{-1} were recorded on a Thermo-electron NXR 9650 FT-Raman spectrometer with an InGaAs detector, CaF$_2$ beamsplitter and 1064 nm Nd:YVO$_4$ laser. Spectra of cyclohexane in a glass sample vial were recorded at 2 cm^{-1} resolution and 25 scans were averaged before FT. Spectra were recorded at both 0.5 and 1.0 W laser power.

3. DFT calculations

The equilibrium geometries, harmonic vibrational frequencies, and infrared and Raman intensities were determined for the chair conformer using the B3LYP functional [10–13] with the 6-311G basis set [14,15]. All DFT calculations were performed using Gaussian 03 [16] on dual core AMD Opteron processors. The harmonic frequencies were scaled by a factor of 0.9614. This is the scaling factor recommended [17] by Scott and Radom for the B3LYP/6-31G(d) method, and so should be a reasonable scaling factor for the B3LYP/6-311G method.[1] The calculated and scaled calculated wavenumbers and IR and Raman intensities are reported in Table 1. The DFT infrared intensities (for gas phase) were converted to liquid phase intensities under the assumption that the dipole moment derivatives are

the same in both phases using the relationship

$$C_{j,liq} = \frac{A_{j,gas}}{(8\pi^2)} \tag{1}$$

as reported by Bertie and Keefe [18]. These integrated intensities were then used with the scaled harmonic wavenumbers to calculate a liquid phase IR absorption spectrum. A full width at half height (FWHH) of 10 cm^{-1} and CDHO lineshape [19] were used for all peaks. The calculated Raman intensities were used with a 10 cm^{-1} FWHH, Lorentzian lineshapes and the scaled harmonic wavenumbers to determine a calculated liquid phase Raman spectrum. These spectra were used to help assign the experimental spectra as discussed below.

4. Results and discussion

The absorption across the infrared varies significantly; in order to be measured accurately the experimental absorbance spectra [6] must be measured in cells with different pathlengths. Experimental absorbance spectra are known to suffer from baseline variations which were corrected using the linear absorption coefficients at anchor points in the baseline [6]. The linear absorption at the anchor points are given in Table S1 and the details concerning the range of pathlengths and the number of spectra recorded in each region are given in Table S2. The experimental absorbance spectra in each region were converted to imaginary refractive index spectra (also called absorption index spectra), $k(\tilde{\nu})$, using the program EXPABS2k. The real refractive indices, $n(\tilde{\nu})$, were calculated from the imaginary refractive indices via the KK transform and from the electronic contribution to the infrared refractive indices [20]. The electronic

---

[1] Calculations were done using both basis sets and on average, the 6-31G(d) frequencies differed from the 6-311G frequencies by 0.08%.