

Available online at www.sciencedirect.com



Journal of Molecular Structure 737 (2005) 207-219

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

# Temperature dependence of the optical properties of liquid toluene between 4000 and 400 cm<sup>-1</sup> from 30 to 105 °C

C. Dale Keefe\*, Shaun Mac Innis

Department of Physical and Applied Sciences, University College of Cape Breton, 1250 Grand Lake Road, Sydney, NS, Canada B1P 6L2

Received 21 June 2004; revised 19 October 2004; accepted 19 October 2004 Available online 26 November 2004

#### Abstract

This paper presents the first systematic study of the temperature dependence of the optical properties of a liquid. The real and imaginary refractive index spectra, and imaginary molar polarizability spectra of toluene were determined from 30 to 105 °C in 5 °C increments. The peak positions, heights and widths all vary linearly with temperature. However, the broadening of the peak width and lowering of the height are in such a manner that the integrated intensities, transition moments and dipole moment derivatives remain constant. Points in the absorption spectra were observed to be independent of temperature. These points have been labeled isoentosic points. © 2005 Elsevier B.V. All rights reserved.

Keywords: Refractive index; Optical constants; Polarizability; Toluene; Liquid; Infrared; Temperature dependence; Absorption index; Dielectric constants

# 1. Introduction

Over the past number of years, this laboratory has been involved in a project to investigate how intermolecular interactions in liquids affect the absolute infrared absorption intensities, i.e. the transition moments or dipole moment derivatives. Previous papers [1–11] have dealt with optical constants of several organic liquids over large portions of the infrared spectrum at room temperature (25 °C). This paper reports new measurements of the optical constants of liquid toluene between 4000 and  $400 \text{ cm}^{-1}$  over a temperature range of 30-105 °C. These optical constants were then used to calculate the dielectric constants, molar absorption coefficients (also referred to as molar absorptivities and extinction coefficients) and the imaginary molar polarizability spectra under the Lorentz local field model. To our knowledge, this is the first ever study of the temperature dependence of the optical constants of an organic liquid.

#### 2. Experimental

The toluene used was HPLC grade purchased from Fisher Scientific. No further purification was done except the toluene was kept over 5A molecular sieve to keep the samples free of water. All experimental absorbance spectra were recorded on a Nicolet Impact 410 FTIR with an Everglo<sup>TM</sup> (Trademark of the Nicolet Instrument Corporation) mid-IR source, a 9 mm aperature, a Ge-on-KBr beamsplitter, and a DTGS detector. A Spectra-Tech HT-32 heated transmission cell regulated by an Omega CN8501 temperature controller with a Chromel–Alumel K-type thermocouple allowed for continuous monitoring of the cell temperature. The cells used 32 mm diameter windows.

Experimental absorbance spectra of toluene were measured with a  $1 \text{ cm}^{-1}$  nominal resolution in fixed pathlength cells with KBr windows and path lengths of 15, 25, 50, 100, and 1000 µm over a temperature range of 30–105 °C in 5 °C intervals. Five-hundred and twelve interferograms were collected for both the background and sample single beam spectra. A background was recorded before each sample. The pathlengths of most of the cells were determined by the program PATHLEN [12], using the fringe patterns in the experimental absorbance spectra of the empty cells. Early on in the study, the pathlengths were

<sup>\*</sup> Corresponding author. Tel.: +1 902 563 1185; fax: +1 902 563 1880. *E-mail address:* dale\_keefe@uccb.ca (C.D. Keefe).

Table 1 Regions processed and pathlengths used for each region

Region	Wavenumber limits $(cm^{-1})$	Pathlengths (µm)
A	4000-3150	1000 <sup>a</sup>
В	3200-2750	15, 25
С	2800-2560	100
D	2565-1970	1000 <sup>b</sup>
Е	2000-1640	50, 100
F	1655–1390	15
G	1420-770	25, 50
Н	780–700	15 <sup>b</sup>
Ι	715-630	15
J	670–475	50, 100
К	510-435	15

<sup>a</sup> The 1000  $\mu$ m cell leaked at 100 and 105 °C and thus for those temperatures, the *k* spectra were determined in a 100  $\mu$ m cell, and the resulting *k* spectra are considerably noisier than at the other temperatures.

<sup>b</sup> An absorption band in this region could not be measured accurately with available pathlengths. The thinnest cell available was used, however, this region was not included in any of the analysis and was only included to complete the spectrum.

measured as a function of temperature, and it was determined that the pathlengths of the cells did not change over the temperature range of the present study. Subsequently, the pathlengths were only determined at 30 °C. For the empty cells which did not give usable fringe patterns, experimental absorbance spectra of benzene were measured and used with the program IRYTRUE [13–15] to calibrate the cell at 25 °C. It was assumed that these cell constants were valid over the entire temperature range.

Since the absorption varies from very weak to very strong across the mid-infrared, the spectrum was broken up

Table 2

Linear absorption	coefficients	at the	anchor	points
-------------------	--------------	--------	--------	--------

into smaller regions. These regions were the same as used by Bertie et al. [10] at 25 °C and are given in Table 1. As discussed in detail in the literature [16–18], each region was then converted to the imaginary refractive index, k, spectrum by the program EXPABS2k [12] from transmission spectra in cells of suitable pathlengths. To properly remove baseline variations, the linear absorption coefficients are needed at anchor points across the spectrum. Bertie et al. [10] determined the linear absorption coefficients very accurately using a wide range of cell pathlengths. Such variety of pathlengths was not available for this study. To determine the temperature dependence of the linear absorption coefficients at the anchor points, values were determined at each temperature using the closest cells to those used by Bertie et al.; the resulting variations were linear with respect to temperature with a very small slope. However, the values extrapolated to 25 °C were not as accurate as Bertie's values, thus the equations were shifted to match Bertie's values at 25 °C. The values of the linear absorption coefficients are shown in Table 2.

The number of spectra processed for each region at each temperature is shown in Table 3. The experimental absorbance spectra were converted to k spectra using EXPABS2k [12] and the linear absorption coefficients at the anchor points given in Table 2. EXPABS2k also requires an approximate value of the real refractive index at the high wavenumber limit of each region. These were calculated at each temperature by converting an experimental absorbance spectrum measured in an 15  $\mu$ m cell to a k spectrum without baseline correction and then to a real refractive index, n, spectrum by KK transformation. These values are shown in

ν̃	Tempe	rature (°C	C)														
$(cm^{-1})$	25 <sup>a</sup>	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105
3970.2	3.94	3.92	3.90	3.88	3.87	3.85	3.83	3.81	3.79	3.77	3.75	3.73	3.72	3.70	3.68	3.66	3.64
3748.0	1.83	1.83	1.83	1.82	1.82	1.82	1.82	1.82	1.82	1.81	1.81	1.81	1.81	1.81	1.80	1.80	1.80
3483.8	1.13	1.13	1.12	1.12	1.11	1.11	1.10	1.10	1.09	1.09	1.08	1.08	1.08	1.07	1.07	1.06	1.06
3355.5	1.56	1.56	1.57	1.57	1.58	1.58	1.59	1.59	1.59	1.60	1.60	1.61	1.61	1.62	1.62	1.62	1.63
3159.3	7.77	7.76	7.75	7.74	7.73	7.72	7.71	7.70	7.69	7.69	7.68	7.67	7.66	7.65	7.64	7.63	7.62
2759.6	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.47	5.47	5.47	5.47	5.47	5.47
2562.9	2.547	2.553	2.559	2.565	2.571	2.577	2.583	2.589	2.595	2.601	2.607	2.613	2.620	2.626	2.632	2.638	2.644
2219.2	1.612	1.621	1.631	1.640	1.650	1.659	1.668	1.678	1.687	1.697	1.706	1.716	1.725	1.734	1.744	1.753	1.763
1977.6	5.97	5.96	5.96	5.95	5.95	5.94	5.94	5.93	5.92	5.92	5.91	5.91	5.90	5.90	5.89	5.89	5.88
1909.7	4.97	5.01	5.05	5.10	5.14	5.18	5.22	5.26	5.30	5.35	5.39	5.43	5.47	5.51	5.55	5.60	5.64
1754.9	6.04	6.05	6.06	6.07	6.08	6.09	6.10	6.12	6.13	6.14	6.15	6.16	6.17	6.18	6.19	6.20	6.21
1648.4	7.79	7.83	7.87	7.91	7.95	7.99	8.03	8.07	8.11	8.15	8.19	8.23	8.27	8.31	8.35	8.39	8.43
1556.3	26.7	26.7	26.8	26.8	26.9	26.9	26.9	27.0	27.0	27.0	27.1	27.1	27.2	27.2	27.2	27.3	27.3
1398.6	33.0	33.1	33.2	33.3	33.4	33.5	33.6	33.7	33.8	33.9	34.0	34.1	34.2	34.3	34.4	34.5	34.6
1231.3	7.49	7.53	7.58	7.62	7.67	7.71	7.76	7.80	7.84	7.89	7.93	7.98	8.02	8.07	8.11	8.16	8.20
919.9	11.11	11.13	11.15	11.17	11.19	11.21	11.23	11.25	11.27	11.29	11.31	11.33	11.35	11.36	11.38	11.40	11.42
776.7	18.1	18.2	18.3	18.4	18.5	18.6	18.6	18.7	18.8	18.9	19.0	19.1	19.2	19.3	19.4	19.5	19.6
708.7	70.2	71.9	73.6	75.4	77.1	78.8	80.5	82.2	84.0	85.7	87.4	89.1	90.9	92.6	94.3	96.0	97.7
636.9	5.07	5.13	5.18	5.24	5.29	5.35	5.41	5.46	5.52	5.58	5.63	5.69	5.74	5.80	5.86	5.91	5.97
508.2	3.99	4.03	4.08	4.12	4.17	4.21	4.26	4.30	4.35	4.39	4.43	4.48	4.52	4.57	4.61	4.66	4.70
436.3	6.21	6.33	6.45	6.56	6.68	6.80	6.92	7.03	7.15	7.27	7.39	7.50	7.62	7.74	7.86	7.97	8.09

<sup>a</sup> From Ref. [10].

Table 3 Number of spectra processed for each region

Temperature (°C)	Region	Region													
	A	В	С	D	Е	F	G	Н	Ι	J	K				
30	6	11	6	6	12	5	12	5	5	11	5				
35	6	11	6	6	12	5	12	5	5	11	5				
40	6	12	6	6	12	6	12	6	6	11	6				
45	5	11	6	5	12	5	12	5	4	10	5				
50	6	10	6	6	12	5	12	5	4	11	4				
55	6	10	6	6	12	4	12	5	3	12	3				
60	6	10	6	6	12	5	12	5	3	12	3				
65	6	11	6	6	12	5	12	5	5	12	5				
70	6	9	6	6	12	5	12	5	4	12	4				
75	6	10	6	6	12	5	12	5	5	12	5				
80	5	10	6	6	12	5	12	5	5	12	5				
85	6	11	6	6	12	6	12	6	6	12	6				
90	6	11	6	6	12	5	12	5	5	12	5				
95	7	10	6	7	12	5	12	5	5	12	5				
100	6	13	6	6	12	7	12	7	7	12	7				
105	6	9	6	6	12	4	12	4	4	12	4				

Table 4. The KK transformation requires n at the high wavenumber limit of the spectrum which in this case is  $4000 \text{ cm}^{-1}$ . These values were obtained from the literature temperature dependence as follows. Timmermans [19] reports the n values at seven visible wavelengths at 20, 25 and 30 °C. At each temperature, the n values were fit to

$$n^{2}(\tilde{\nu}) = a_{0}(T) + a_{2}(T)\tilde{\nu}^{2} + a_{4}(T)\tilde{\nu}^{4}$$
(1)

The literature values and fitted curves are shown in Fig. 1. The resulting coefficients  $a_i$  (i=0, 2, 4) were fit to the linear equation

$$a_i(T) = b_{i,0} + b_{i,1}T \tag{2}$$

giving

$$a_0(T) = 2.20954 - 1.592 \times 10^{-3} T/^{\circ} C,$$

$$a_2(T) = 1.994 \times 10^{-10} \text{ cm}^2 - 3.105 \times 10^{-13} \text{ cm}^2 T/^{\circ} C,$$
(4)

$$a_4(T) = 9.353 \times 10^{-20} \text{ cm}^4 - 1.625 \times 10^{-22} \text{ cm}^4 T/^{\circ}\text{C}.$$
(5)

The fitting parameters are shown in Fig. 2. The coefficients for Eq. (1) and the  $n_{4000}$  values are shown in Table 5 at each temperature.

At each temperature, the k spectra for each region were averaged and the regions merged together to give a full

Table 4 Real refractive index at the upper wavenumber limit in each region

Temperature (°C)	$\tilde{\nu} (\mathrm{cm}^{-1})$												
	4000.1	3170.4	2775.0	2565.3	2000.3	1655.1	1420.3	780.1	715.5	670.1	510.1		
30	1.4673	1.4774	1.4884	1.4857	1.4820	1.4782	1.4965	1.4630	1.6196	1.5846	1.5356		
35	1.4644	1.4756	1.4867	1.4839	1.4802	1.4763	1.4938	1.4672	1.6141	1.5805	1.5343		
40	1.4613	1.4741	1.4853	1.4826	1.4792	1.4761	1.4938	1.4580	1.6153	1.5802	1.5328		
45	1.4588	1.4710	1.4808	1.4784	1.4754	1.4726	1.4885	1.4572	1.5986	1.5672	1.5276		
50	1.4561	1.4673	1.4784	1.4758	1.4721	1.4691	1.4866	1.4500	1.6149	1.5783	1.5259		
55	1.4535	1.4643	1.4754	1.4728	1.4691	1.4667	1.4833	1.4472	1.6074	1.5718	1.5208		
60	1.4508	1.4614	1.4725	1.4699	1.4663	1.4657	1.4798	1.4486	1.5986	1.5641	1.5147		
65	1.4481	1.4586	1.4697	1.4670	1.4633	1.4605	1.4773	1.4418	1.6025	1.5664	1.5152		
70	1.4453	1.4566	1.4670	1.4646	1.4612	1.4591	1.4740	1.4414	1.5836	1.5531	1.5074		
75	1.4428	1.4527	1.4631	1.4604	1.4567	1.4516	1.4690	1.4432	1.5849	1.5529	1.5096		
80	1.4397	1.4513	1.4613	1.4589	1.4557	1.4525	1.4682	1.4375	1.5821	1.5489	1.5068		
85	1.4372	1.4473	1.4582	1.4556	1.4519	1.4483	1.4650	1.4299	1.5811	1.5468	1.4986		
90	1.4342	1.4458	1.4561	1.4537	1.4499	1.4452	1.4615	1.4371	1.5743	1.5470	1.5018		
95	1.4320	1.4413	1.4509	1.4485	1.4453	1.4427	1.4566	1.4297	1.5650	1.5352	1.4941		
100	1.4289	1.4391	1.4504	1.4477	1.4439	1.4410	1.4567	1.4223	1.5742	1.5429	1.4914		
105	1.4257	1.4385	1.4475	1.4454	1.4423	1.4368	1.4530	1.4314	1.5473	1.5278	1.4928		



Fig. 1. The electronic contributions to the real refractive index of liquid toluene at 20, 25 and 30 °C. The experimental data are from Ref. [19]. The diamonds are data at 20 °C, the squares are data at 25 °C, the crosses are data at 30 °C and the solid curves were determined from Eq. (1).

range spectrum (4000–400 cm<sup>-1</sup>). The average imaginary refractive index spectra were KK transformed to obtain the real refractive index spectra. The *k* and *n* spectra at 30 °C are shown in Figs. 3 and 4, respectively. The spectra at the other temperatures are not shown. It has been estimated [10] that *k* spectra determined in this manner have an uncertainty of approximately 2–3% and the corresponding *n* spectra have an uncertainty of approximately 0.2%.

Other optical quantities, such as the molar absorption coefficient  $(E_m)$ , the complex dielectric constants  $(\hat{\varepsilon} = \varepsilon' + i\varepsilon'')$ , the complex molar polarizability  $(\hat{\alpha}_{\rm m} = \alpha'_{\rm m} + i\alpha''_{\rm m})$ , and the wavenumber times imaginary molar polarizability  $(\tilde{\nu}\alpha''_m)$  spectra, can be calculated from the complex refractive index spectra using equations in the literature [20]. The real components have a similar uncertainty as the real refractive index and the imaginary components have a similar uncertainty as the imaginary refractive index. The areas under the wavenumber times imaginary molar polarizability spectra are estimated [10] to have an uncertainty of about 2.4%. The complete spectra are available in digital form from CDK's website (http://faculty.uccb.ns.ca/dkeefe/spectra). For the current study, the imaginary molar polarizability spectra are the principle spectra of interest. The imaginary molar polarizability spectrum at 30 °C is shown in Fig. 5.



Fig. 2. The temperature dependence of the coefficients of Eq. (1). The diamonds are for  $a_0$ , the squares are for  $10^{10} a_2$  and the triangles are for  $10^{20} a^4 - 8$ .

## 3. Results and discussion

The temperature variations in the imaginary molar polarizability spectra are illustrated for various regions in Figs. 6–8 for 30, 55, 80 and 105 °C. For clarity the other temperatures are not shown. One of the interesting features of the plots is that there are points where all the spectra have the same imaginary polarizability value at the various temperatures. For example, in the top box of Fig. 6, such

Table 5 Coefficients for Eq. (1) and  $n_{4000}$  at each temperature

Temperature (°C)	$a_0$	$a_2 ({\rm cm}^2)$	$a_4 ({\rm cm}^4)$	<i>n</i> 4000
$\frac{(c)}{30}$	2 16170	$1.90 \times 10^{-10}$	$8.87 \times 10^{-20}$	1 /713
35	2.15383	$1.90 \times 10$ $1.89 \times 10^{-10}$	$8.78 \times 10^{-20}$	1.4686
40	2.14587	$1.87 \times 10^{-10}$	$8.70 \times 10^{-20}$	1.4659
45	2.13791	$1.85 \times 10^{-10}$	$8.62 \times 10^{-20}$	1.4632
50	2.12995	$1.84 \times 10^{-10}$	$8.54 \times 10^{-20}$	1.4605
55	2.12199	$1.82 \times 10^{-10}$	$8.46 \times 10^{-20}$	1.4577
60	2.11403	$1.81 \times 10^{-10}$	$8.38 \times 10^{-20}$	1.4550
65	2.10608	$1.79 \times 10^{-10}$	$8.30 \times 10^{-20}$	1.4522
70	2.09812	$1.78 \times 10^{-10}$	$8.21 \times 10^{-20}$	1.4495
75	2.09016	$1.76 \times 10^{-10}$	$8.13 \times 10^{-20}$	1.4467
80	2.08220	$1.75 \times 10^{-10}$	$8.05 \times 10^{-20}$	1.4440
85	2.07424	$1.73 \times 10^{-10}$	$7.97 \times 10^{-20}$	1.4412
90	2.06628	$1.71 \times 10^{-10}$	$7.89 \times 10^{-20}$	1.4384
95	2.05832	$1.70 \times 10^{-10}$	$7.81 \times 10^{-20}$	1.4356
100	2.05037	$1.68 \times 10^{-10}$	$7.73 \times 10^{-20}$	1.4329
105	2.04241	$1.67 \times 10^{-10}$	$7.65 \times 10^{-20}$	1.4301



Fig. 3. The imaginary refractive index spectrum of liquid toluene at 30 °C. The upper curve in each box is multiplied by 10.



Fig. 4. The real refractive index spectrum of liquid toluene at 30 °C.



Fig. 5. The imaginary molar polarizability spectrum of liquid toluene at 30 °C in cm<sup>3</sup> mol<sup>-1</sup>. The upper curve in each box is multiplied by 10.

points appear at just above 3030 and just below  $3020 \text{ cm}^{-1}$ . These points are similar in concept to the isosbestic points observed when measuring spectra of varying composition. We have not been able to find a similar term in the chemical literature to describe these points and to our knowledge this is the first time they have ever been observed. We are suggesting the term *isoentosic* points, from the Greek for equal intensity, to indicate points where the absorption is independent of temperature. Similar points also appear in the other absorption spectra, such as the imaginary refractive index, molar absorption coefficient and dielectric loss spectra, but the actual wavenumber location may vary and they are the most obvious in the imaginary molar polarizability and molar absorption coefficient spectra. Some of the isoentosic points observed in the imaginary molar polarizability spectra were not observed in the imaginary refractive index or imaginary dielectric constant spectra.

The peak positions for 12 of the peaks in the imaginary molar polarizability spectra of liquid toluene are given in Table 6 for the temperatures measured in this study and the corresponding peak heights in the imaginary molar polarizability spectra are given in Table 7. The peak positions and heights were determined by parabolic interpolation of the three highest data points of each peak via PEAKINFO.<sup>1</sup> The peak positions are plotted as a function of temperature in Figs. 9–11. It is obvious from the figures that the peak positions vary linearly with temperature, although the amount is relatively small but nonetheless significant. For 9 of the 12 peaks the peak position decreases with temperature.

The peak heights are plotted as a function of temperature in Figs. 12–14. The peak heights also vary linearly with temperature. However, there is more scatter from the fitted line than with the peak positions. This is due to the fact that the positions are known much more accurately than the heights. For the 12 peaks, all of the peak heights decrease with temperature. The peak heights decrease by at least 6% over the 75 °C temperature range studied and for 7 of the 12 peaks the peak heights decrease by more than 20% with the 1604 cm<sup>-1</sup> peak height decreasing by 44%.

The widths, expressed as the full-width-at-half-height (FWHH), for eight of these peaks are given in Table 8. The FWHH for the other four peaks could not be determined

<sup>&</sup>lt;sup>1</sup> Available from CDK's website (http://faculty.uccb.ns.ca/dkeefe/programs).



Fig. 6. The imaginary molar polarizability spectra of liquid toluene at 30, 55, 80 and 105  $^{\circ}$ C in cm<sup>3</sup> mol<sup>-1</sup>. In each box, the peaks from highest to lowest are for 30, 55, 80 and 105  $^{\circ}$ C, respectively.

accurately due to overlap with neighbouring peaks. The peak widths, plotted as a function of temperature in Figs. 15 and 16, increase with temperature. The peak widths increase by at least 16% over the 75 °C temperature range studied and for seven peaks the width increases by more than 30%.

Noting that the peak heights decrease linearly with temperature and the corresponding widths increase linearly with temperature, the next obvious question is 'How do the integrated intensities change with temperature?'. When studying liquids, the preferred [20] integrated intensity is the area under the wavenumber times the imaginary molar polarizability (referred to as  $C_j$ ) which is related to the square of the dipole moment derivative and the square of the transition moment. The  $C_j$  areas are given for six regions considered in this paper in Table 9 and are plotted in Fig. 17. While the peak heights vary by as much as 44% and the widths by as much as 48%, the maximum variation from

the largest to smallest of the areas for any one region is 14%. The maximum deviations from the average areas for the regions are on the order of 7% or less and the standard deviations from the averages are 4% or less. This variation of the areas is on the order of the uncertainty of the areas themselves. Thus, within the current accuracy of the areas, the areas do not depend on temperature. Corresponding, the transition moments and dipole moment derivatives, which are related to the square root of  $C_i$ , can also be considered to be independent of temperature. In this study, no attempt has been made to separate the contributions to the areas of individual transitions in regions of overlap such as the CH stretch region. However, given the amount of variation in the integrated intensity, calculated as the area under the curve between given limits, of the bands that are fairly isolated from other major peaks, it is expected that the individual contributions will also remain unchanged in regions of overlap.



Fig. 7. The imaginary molar polarizability spectra of liquid toluene at 30, 55, 80 and 105  $^{\circ}$ C in cm<sup>3</sup> mol<sup>-1</sup>. In each box, the peaks from highest to lowest are for 30, 55, 80 and 105  $^{\circ}$ C, respectively.



Fig. 8. The imaginary molar polarizability spectra of liquid toluene at 30, 55, 80 and 105  $^{\circ}$ C in cm<sup>3</sup> mol<sup>-1</sup>. In each box, the peaks from highest to lowest are for 30, 55, 80 and 105  $^{\circ}$ C, respectively.

 Table 6

 Peak positions in the imaginary molar polarizability spectra of liquid toluene

Temperature (°C)	$\tilde{\nu} (\mathrm{cm}^{-1})$											
30	3085.91	3061.40	3026.70	2919.33	1604.31	1495.13	1459.52	1378.84	1081.30	1029.98	694.51	464.28
35	3085.89	3061.64	3026.57	2919.42	1604.27	1495.11	1459.38	1378.87	1081.28	1029.96	694.41	464.23
40	3085.82	3061.45	3026.85	2919.59	1604.25	1495.12	1459.32	1378.90	1081.25	1029.96	694.35	464.19
45	3085.82	3061.56	3026.93	2920.01	1604.21	1495.11	1457.08	1378.96	1081.20	1029.95	694.35	464.13
50	3085.81	3061.20	3026.83	2919.75	1604.16	1495.11	1457.08	1378.99	1081.17	1029.94	694.36	464.11
55	3085.79	3061.34	3026.87	2920.10	1604.13	1495.10	1457.10	1379.03	1081.13	1029.92	694.33	464.10
60	3085.61	3061.35	3026.93	2920.25	1604.10	1495.06	1459.43	1379.08	1081.09	1029.91	694.28	464.07
65	3085.55	3061.54	3027.15	2920.12	1604.04	1495.06	1457.08	1379.10	1081.04	1029.90	694.19	463.99
70	3085.54	3061.44	3027.01	2920.43	1603.96	1495.07	1456.99	1379.14	1080.99	1029.89	694.18	463.93
75	3085.47	3061.51	3027.10	2920.47	1603.92	1495.08	1456.95	1379.17	1080.96	1029.87	694.10	463.87
80	3085.41	3061.18	3027.16	2920.42	1603.89	1495.04	1457.02	1379.19	1080.93	1029.87	694.08	463.85
85	3085.37	3061.39	3027.14	2920.58	1603.79	1495.07	1456.88	1379.24	1080.86	1029.84	694.08	463.83
90	3085.17	3061.31	3027.21	2920.73	1603.78	1495.02	1456.97	1379.27	1080.83	1029.83	694.05	463.79
95	3085.09	3061.14	3027.14	2920.81	1603.69	1495.03	1456.98	1379.28	1080.77	1029.82	693.99	463.75
100	3085.01	3061.44	3027.31	2921.01	1603.72	1494.98	1455.19	1379.31	1080.72	1029.81	693.95	463.68
105	3084.93	3060.94	3027.30	2921.03	1603.56	1495.03	1456.93	1379.34	1080.69	1029.79	693.93	463.59

Table 7
Peak heights in the imaginary molar polarizability spectra of liquid toluene

Temperature (°C)	$\alpha''_{\rm m}(\tilde{\nu})$ (cm	$\alpha''_{\rm m}(\tilde{\nu})  ({\rm cm}^3  {\rm mol}^{-1})$													
	3085	3061	3027	2920	1604	1495	1459	1379	1081	1030	694	464			
30	0.143	0.169	0.372	0.210	0.402	1.36	0.364	0.167	0.376	0.511	4.07	3.54			
35	0.143	0.172	0.376	0.210	0.383	1.30	0.351	0.166	0.370	0.508	3.91	3.34			
40	0.144	0.171	0.372	0.206	0.365	1.25	0.339	0.164	0.361	0.496	3.82	3.23			
45	0.139	0.173	0.372	0.203	0.353	1.22	0.332	0.161	0.350	0.485	3.68	3.17			
50	0.138	0.170	0.368	0.205	0.353	1.22	0.339	0.160	0.341	0.475	3.61	3.17			
55	0.143	0.170	0.367	0.202	0.356	1.23	0.342	0.159	0.335	0.467	3.68	3.17			
60	0.136	0.169	0.363	0.202	0.336	1.15	0.326	0.157	0.330	0.461	3.40	3.05			
65	0.134	0.173	0.368	0.203	0.325	1.12	0.321	0.157	0.321	0.451	3.45	2.93			
70	0.139	0.168	0.357	0.200	0.290	1.01	0.303	0.157	0.318	0.446	3.27	2.83			
75	0.138	0.173	0.363	0.201	0.299	1.04	0.317	0.157	0.311	0.439	3.26	2.72			
80	0.137	0.173	0.362	0.202	0.297	1.03	0.310	0.157	0.308	0.435	3.18	2.69			
85	0.138	0.175	0.364	0.204	0.289	1.02	0.320	0.155	0.302	0.427	3.20	2.68			
90	0.142	0.182	0.378	0.211	0.301	1.04	0.322	0.154	0.296	0.419	3.21	2.73			
95	0.136	0.174	0.360	0.201	0.276	0.96	0.302	0.153	0.292	0.415	3.04	2.53			
100	0.141	0.181	0.369	0.207	0.278	0.94	0.304	0.153	0.287	0.406	2.95	2.50			
105	0.137	0.175	0.356	0.199	0.260	0.90	0.302	0.151	0.280	0.397	2.85	2.41			



Fig. 9. The peak positions in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The solid diamonds are for the  $3080 \text{ cm}^{-1}$  peak, the solid squares the 3060 peak, the solid triangles the 3026 peak and the open circles for the  $2920 \text{ cm}^{-1}$  peak.



Fig. 10. The peak positions in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The crosses are for the  $1605 \text{ cm}^{-1}$  peak, the open squares the 1495 peak, the open triangles the 1459 peak and the solid circles for the  $1379 \text{ cm}^{-1}$  peak.



Fig. 11. The peak positions in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The open diamonds are for the  $1081 \text{ cm}^{-1}$  peak, the asterisks the 1029 peak, the triangles the 695 peak and the circles for the 465 cm<sup>-1</sup> peak.



Fig. 12. The peak heights in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The solid diamonds are for the  $3080 \text{ cm}^{-1}$  peak, the solid squares the 3060 peak, the solid triangles the 3026 peak and the open circles for the  $2920 \text{ cm}^{-1}$  peak.



Fig. 13. The peak heights in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The crosses are for the  $1605 \text{ cm}^{-1}$  peak, the open squares the 1495 peak, the open triangles the 1459 peak and the solid circles for the  $1379 \text{ cm}^{-1}$  peak.



Fig. 14. The peak heights in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The open diamonds are for the  $1081 \text{ cm}^{-1}$  peak, the asterisks the 1029 peak, the triangles the 695 peak and the circles for the 465 cm<sup>-1</sup> peak.

Table 8 Peak widths in the imaginary molar polarizability spectra of liquid toluene

Tempera-	$\tilde{\nu} (\mathrm{cm}^{-1})$												
ture (°C)	3027	1604	1495	1379	1081	1030	694	464					
30	22.04	6.81	5.19	13.18	9.41	5.04	4.95	4.51					
35	22.29	7.05	5.37	13.37	9.65	5.13	5.01	4.67					
40	22.62	7.33	5.51	13.71	9.97	5.27	5.04	4.78					
45	22.79	7.62	5.67	14.96	10.25	5.36	5.27	4.84					
50	22.56	7.88	5.84	15.04	10.57	5.49	5.45	4.91					
55	22.75	8.28	6.06	15.22	10.99	5.68	5.51	4.92					
60	22.86	8.56	6.24	15.33	11.45	5.87	5.76	4.99					
65	23.26	8.64	6.30	15.74	11.80	6.04	5.73	5.13					
70	23.36	8.81	6.45	16.03	12.21	6.22	5.99	5.21					
75	23.91	9.07	6.69	16.28	12.51	6.36	5.92	5.42					
80	24.05	9.49	6.88	16.62	12.91	6.55	6.12	5.39					
85	24.29	9.40	6.97	16.78	13.35	6.72	6.21	5.54					
90	24.43	9.96	7.22	17.04	13.78	6.94	6.41	5.61					
95	24.72	10.34	7.39	17.32	14.16	7.12	6.48	5.71					
100	25.38	10.88	7.70	19.39	14.59	7.36	6.74	5.86					
105	25.80	10.78	7.97	17.98	15.15	7.60	6.89	5.98					

#### 4. Summary

This paper presents the first systematic study of the temperature dependence of the optical properties of a liquid. The real and imaginary refractive index spectra, and imaginary molar polarizability spectra of toluene were determined from 30 to  $105 \,^{\circ}$ C in 5  $^{\circ}$ C increments. It was determined that the peak position, peak height and peak



Fig. 15. The FWHH of the peaks in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The solid triangles are for the  $3026 \text{ cm}^{-1}$  peak, the crosses the 1065 peak, the open triangles the 1459 peak and the solid circles for the 1379 cm<sup>-1</sup> peak.



Fig. 16. The FWHH of the peaks in the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The asterisks are for the  $1029 \text{ cm}^{-1}$  peak, the triangles the 695 peak and the circles for the 465 cm<sup>-1</sup> peak.

width all vary linearly with temperature. However, the broadening of the peak width and lowering of the height are in such a manner that within the current accuracy of the measurements, no systematic variation in the areas can be observed. Thus, the transition moments and dipole moment derivatives are considered to be independent of temperature.

Table 9

Areas under the wavenumber times imaginary molar polarizability spectra of liquid toluene

Tem-	$C_j  (\mathrm{km  mol}^{-1})$											
perature (°C)	3150.1– 2770.2	1650.3– 1555.3	1513.3– 1400.1	1265.6– 821.0	710.2– 660.0	490.3– 440.2						
30	1.05	0.105	0.389	0.285	0.227	0.107						
35	1.06	0.104	0.380	0.283	0.222	0.105						
40	1.06	0.103	0.372	0.283	0.220	0.105						
45	1.05	0.103	0.370	0.280	0.220	0.104						
50	1.04	0.105	0.376	0.279	0.222	0.105						
55	1.04	0.109	0.387	0.281	0.230	0.106						
60	1.03	0.107	0.374	0.285	0.223	0.105						
65	1.05	0.104	0.366	0.284	0.225	0.103						
70	1.03	0.095	0.338	0.287	0.223	0.100						
75	1.05	0.099	0.353	0.286	0.221	0.099						
80	1.05	0.102	0.356	0.289	0.222	0.100						
85	1.06	0.098	0.353	0.288	0.227	0.102						
90	1.10	0.105	0.369	0.289	0.232	0.105						
95	1.05	0.102	0.349	0.290	0.224	0.100						
100	1.10	0.105	0.356	0.290	0.226	0.101						
105	1.06	0.097	0.341	0.290	0.223	0.099						



Fig. 17. The areas under the wavenumber times the imaginary molar polarizability spectra of liquid toluene as a function of temperature. The solid squares are the areas under the curve between 3150.1 and 2770.2 cm<sup>-1</sup>, the crosses the areas between 1513.3 and 1400.1, the solid triangles the areas between 1265.6 and 821.0, the solid circles the areas between 710.2 and 660.0, the open circles the areas between 490.3 and 440.3 and the solid diamonds the areas between 1650.3 and 1555.3 cm<sup>-1</sup>. Note that the open circles overlap with the solid diamonds.

At this stage, the processes behind the peak shifts, and the independence of the transition moments on temperature are not fully understood and will require more work.

It was observed that the absorption spectra show points where the absorption is independent of temperature. These points have been labeled isoentosic points.

## Acknowledgements

The authors thank the Natural Sciences & Engineering Research Council of Canada and the office of Research and Academic Institutes at the University College of Cape Breton for their support of this research. The authors thank Prof. George Karaphillis of the UCCB School of Business for suggesting the term isoentosic.

# References

- [1] C.D. Keefe, E. Brand, J. Mol. Struct. 691 (2004) 181.
- [2] C.D. Keefe, L.A. Donovan, J. Mol. Struct. 597 (2001) 259.

- [3] C.D. Keefe, L.A. Donovan, S.D. Fleet, J. Phys. Chem. A 103 (1999) 6420.
- [4] C.D. Keefe, S. MacInnis, T. Burchell, J. Mol. Struct. 610 (2002) 253.
- [5] C.D. Keefe, J.K. Pearson, A. MacDonald, J. Mol. Struct. 655 (2003) 69.
- [6] C.D. Keefe, J. Pittman, Appl. Spectrosc. 52 (1998) 1062.
- [7] C.D. Keefe, Absolute Infrared Absorption Intensities of Liquid Benzene. PhD Thesis, Alberta, 1994.
- [8] J.E. Bertie, C.D. Keefe, J. Mol. Struct. 695-696C (2004) 39.
- [9] J.E. Bertie, R.N. Jones, C.D. Keefe, Appl. Spectrosc. 47 (1993) 891.
- [10] J.E. Bertie, R.N. Jones, Y. Apelblat, C.D. Keefe, Appl. Spectrosc. 48 (1994) 127.
- [11] J.E. Bertie, Y. Apelblat, C.D. Keefe, Infrared Intensities of Liquids XXV: Integrated Intensities of Liquid Toluene at 25 °C, in preparation.
- [12] C.D. Keefe, J. Mol. Struct. 641 (2002) 165.

- [13] J.E. Bertie, C.D. Keefe, R.N. Jones, Tables of Intensities for the Calibration of Infrared Spectroscopic Measurements in the Liquid Phase, Blackwell Scientific Publications, Oxford, 1995.
- [14] J.E. Bertie, S.L. Zhang, R.N. Jones, Y. Apelblat, C.D. Keefe, Appl. Spectrosc. 49 (1995) 1821.
- [15] J.E. Bertie, C.D. Keefe, R.N. Jones, H.H. Mantsch, D.J. Moffatt, Appl. Spectrosc. 45 (1991) 1233.
- [16] J.E. Bertie, C.D. Keefe, R.N. Jones, Can. J. Chem. 69 (1991) 1609.
- [17] J.E. Bertie, S.L. Zhang, C.D. Keefe, Vib. Spectrosc. 8 (1995) 215.
- [18] T.G. Goplen, D.G. Cameron, R.N. Jones, Appl. Spectrosc. 34 (1980) 657.
- [19] J. Timmermans, Toluene, vol. 2 Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1965. pp. 101.
- [20] J.E. Bertie, S.L. Zhang, C.D. Keefe, J. Mol. Struct. 324 (1994) 157.