Near Infrared Absorption of Pure n-Heptane between 5000 cm^{-1} and 6500 cm^{-1} to High Pressures and Temperatures

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The near infrared absorption of pure n-heptane between 5000 cm^{-1} and 6500 cm^{-1} was measured up to 250 °C and to pressures of 2000 bar. The procedure for measuring vibrational intensities at high pressures and temperatures with a precision of better than ± 1% is described. The integrated molar absorptivity of the combination mode $\nu_a + \nu_s$ of the methylene stretching fundamentals turns out to be independent of temperature and density. This offers important applications for high-pressure high-temperature thermodynamic and kinetic studies via quantitative near infrared spectroscopy.

Introduction

Infrared experiments in an extended pressure and temperature range provide information about the structure and dynamics in fluids. In recent years, special interest has developed in the study of vibrational intensities as it turned out that concentrations may be determined at high pressures and temperatures via quantitative infrared and near infrared spectroscopy [1–3]. The new technique proved to be well suited for kinetic and thermodynamic work on the ethylene-polyethylene system [4–6]. It seems desirable to perform absorption experiments on other materials with special emphasis on the validity of Lambert-Beer's law at high pressures and temperatures, which constitutes the basic requirement for the application of the quantitative spectroscopic method. Near infrared experiments [1, 2] are especially important as, even with pure materials, optical layers in the order of millimeters may be used compared to layers of micron size in the fundamental region. It was the aim of this work to measure the absorption of n-heptane between 5000 cm^{-1} and 6500 cm^{-1} to 2 kbar and to 250 °C. An important question centers around the accuracy of absorption intensity measurements at high pressures and temperatures.

Experimental

The cylindrical stainless steel (Remanit 1740, DEW) optical cell [6], for operation to 2 kbar and 300 °C, is shown in Figure 1. The sapphire windows W are sealed against the polished surface of two conical steel plugs P (ATS 340, DEW) which are pressed against the cell body with flanges Fl by means of eight screws S on each side. The cell is heated (H) electrically from outside. The temperature is measured with a sheathed thermocouple St introduced into the internal volume. The cell is charged through a second cross-bore into which a capillary tube is fitted. (The notations I, II, and III in Fig. 1 are explained in the subsequent chapter.)

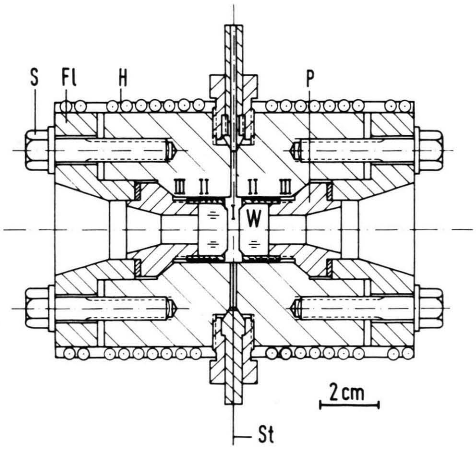

Fig. 1. Optical high-pressure cell. S screw, Fl flange, H heating, P plug, W sapphire window, St sheathed thermocouple.

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Temperatures are measured within the high-pressure fluid to better than ± 0.5 °C. The maximum error in pressure is ± 2.5 bar. The n-heptane densities which were obtained from published PVT-data [7] are accurate within ± 0.5%.

The near infrared spectra were measured on a Fourier-transform spectrometer (DIGILAB FTS 14) which plots the molar absorptivity ε as a function of the wavenumber $\bar{\nu}$. $\varepsilon(\bar{\nu})$ is defined as:

$$\varepsilon(\bar{\nu}) = A(\bar{\nu})/c\,l\,, \qquad (1)$$

$A(\bar{\nu}) = \log_{10}(I_R(\bar{\nu})/I_S(\bar{\nu}))$ is the absorbance; $I_R(\bar{\nu})$ and $I_S(\bar{\nu})$ are the reference and sample beam intensities, respectively. c is the actual n-heptane concentration (or density) in moles per unit volume and l is the optical path length. The precision of the reported molar absorptivities ε and of the integrated molar absorptivities $B = \int \varepsilon(\bar{\nu})\,d\bar{\nu}$ is essentially limited through uncertainties in the knowledge of the optical path length l as will be discussed in the subsequent text. The accuracy of ε and B, in addition, depends on the proper choice of the base-line.

Results and Discussion

The molar absorptivity ε of pure n-heptane from 6500 cm^{-1} to 5000 cm^{-1} is shown in Fig. 2 for pressures between 50 bar and 2000 bar at 150 °C. The n-heptane density decreases from 0.731 g · cm^{-3} at 2000 bar to 0.574 g · cm^{-3} at 50 bar. An essential problem in near infrared spectroscopy relates to the proper assignment of the observed bands which is especially true for polyatomic molecules. The weak components at 5908 cm^{-1} and 5870 cm^{-1} are due to CH_3-vibrations. Both components almost disappear in the spectrum of long-chain n-alcanes, such as n-hexadecane. The intense bands at about 5804 cm^{-1} and 5675 cm^{-1} (Fig. 2) which are slightly shifted with the length of the methylene sequence, dominate the n-hexadecane spectrum. From this observation and from group-theoretical arguments, the following assignments for the n-heptane near infrared spectrum are made [8]: The 5804 cm^{-1} band is the combination mode $\nu_a + \nu_s$ of the asymmetric (ν_a) and symmetric (ν_s) C–H stretching fundamentals of the CH_2-group. The 5675 cm^{-1} band is $2\nu_A$, the first overtone of ν_A. Assignments of this type, based on group vibrations instead of normal modes, obviously are approximate solutions of the vibrational problem. Further arguments related to the band assignment are presented elsewhere [1, 8].

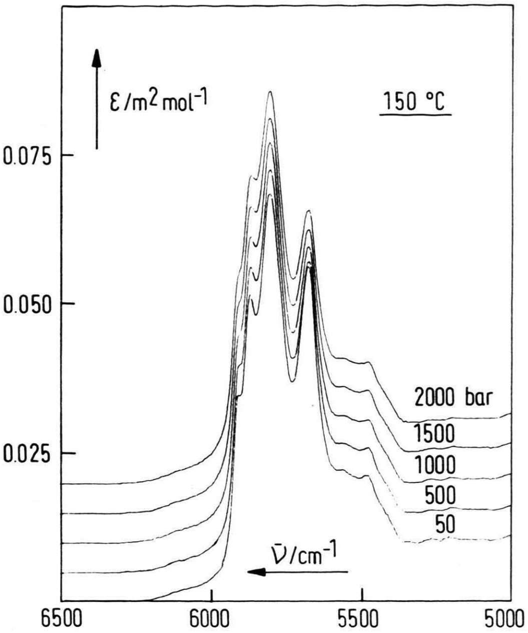

Fig. 2. Molar absorptivity ε/m^2 mol^{-1} of pure n-heptane in the wavenumber region from 5000 cm^{-1} to 6500 cm^{-1} for various pressures at 150 °C.

The molar absorptivity curves in Fig. 2 have been shifted in the base-line in order to avoid strong intersection of the spectra. The precision in ε, if one neglects uncertainties due to the different index of refraction for sample and reference, is essentially limited through the imprecise knowledge of the path length l in (1). For the data in Fig. 2, l is calculated from $l_0 = 1.880$ mm, the optical path length calibrated at ambient temperature and pressure, with additional terms $\Delta l'(T) = 6.4\ \mu$m/100 °C and $\Delta l'(P) = 1.5\ \mu$m/100 bar, which correct for the dependence of l on temperature and pressure. These correction terms have been determined by Heym [5] for a similar, but somewhat smaller optical high-pressure cell. As they may not be completely adequate for the cell in Fig. 1, the path length problem has to be considered in more detail: The temperature dependence of l may be found from a closer inspection of the regions I, II, and III between the conical seals of the steel plugs in Figure 1. The variation of path length is determined by the thermal expansion of the cell body versus the thermal expansion of the steel plugs and the sapphire windows. With the coefficients of thermal expansion: α (Remanit 1740) = 11 · 10^{-6} K^{-1}, α (ATS 340)

$= 12{,}75 \cdot 10^{-6}\,\mathrm{K}^{-1}$, and α (sapphire) $= 5.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$ and with the lengths of the regions I, II, and III being 1.88 mm, $2 \cdot 10$ mm, and $2 \cdot 10$ mm, respectively, the variation with temperature of the path length for the optical cell in Fig. 1 is obtained to be $\Delta l(T) = 9\ \mu\mathrm{m}/100\ °\mathrm{C}$. Using this correction, the integrated molar absorptivity $B_\mathrm{T} = \int \varepsilon_\mathrm{T}(\bar{\nu})\,\mathrm{d}\bar{\nu}$ is calculated for the high wavenumber half-band from 6300 cm^{-1} to the band maximum $\bar{\nu}$(max) which is positioned between 5804 cm^{-1} and 5808 cm^{-1} depending on the experimental temperature. The notation B_T indicates that the optical path has only been corrected for the actual temperature whereas the pressure refers to one atmosphere.

A striking feature of the data in Table 1 is that $B_\mathrm{T}(6300-\bar{\nu}(\max))$, at constant pressure, does not depend on temperature. The mean values (in $\mathrm{km \cdot mol^{-1}}$) are: 0.685 ± 0.005 at 50 bar, 0.691 ± 0.002 at 500 bar, 0.704 ± 0.001 at 1000 bar, 0.716 ± 0.002 at 1500 bar, and 0.722 ± 0.008 at 2000 bar. The small standard deviation, e.g. 0.704 ± 0.001 for six temperatures from 30 °C to 250 °C at 1 kbar, demonstrates the high precision of the absorption experiments. As the n-heptane density varies along each of these isobars, the numbers seem to indicate that the integrated molar absorptivity in the region from 6300 cm^{-1} to $\bar{\nu}$(max) is independent of temperature and of density. Assuming this to be true within the whole experimental pressure and temperature range, the mean values of $B_\mathrm{T}(6300-\bar{\nu}(\max))$ are used to derive the pressure dependence of the optical path length $\Delta l(P)$ for the cell in Figure 1. From the straight line fit of the mean values of $B_\mathrm{T}(6300-\bar{\nu}(\max))$ in Fig. 3, $\Delta l(P)$ is obtained to be $6.4 \pm 0.4\ \mu\mathrm{m}/100$ bar. At 200 °C and 2 kbar, the optical path length is by 143 μm, corresponding to 7.7%, larger than at ordinary temperature and pressure ($l_0 = 1880\ \mu\mathrm{m}$). This variation, which mainly results from the pressure effect, is calculated from $\Delta l(T)$ and $\Delta l(P)$ within ± 6.5%. Thus for optical layers of about 2 mm, up to 200 °C and 2 kbar (for an accurately measured value of l_0), l is known to better than ± 0.6%, and determinations of integrated intensities at high pressures and temperatures to better than ± 1% are within reach.

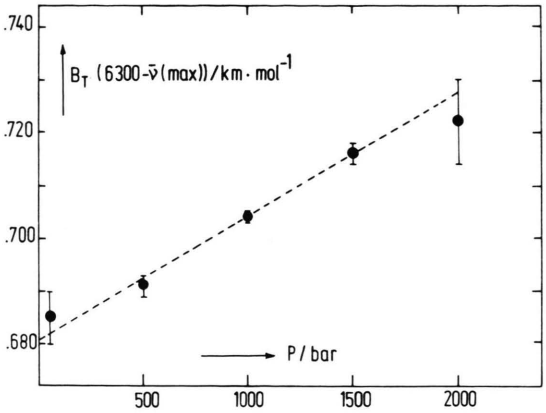

Fig. 3. Integrated molar absorptivity $B_\mathrm{T}(6300-\bar{\nu}(\max))/$ $\mathrm{km \cdot mol^{-1}}$ of pure n-heptane plotted versus pressure. B_T is calculated using an optical path length which has been corrected for the actual temperature but refers to one bar (see text).

Table 1. Integrated molar absorptivity $B_\mathrm{T}(6300-\bar{\nu}(\max))$ in the near infrared spectrum of pure n-heptane at temperatures between 30 °C and 250 °C and for pressures from 50 bar to 2000 bar. B_T differs from final intensities B, as in Table 2, in that the optical path length has only been corrected for the actual temperature while it refers to the calibration pressure of one atmosphere. The experimental data for $\bar{\nu}$(max) are: 5804 cm^{-1} at 30 °C, 5805 cm^{-1} at 50 °C, 5806 cm^{-1} at 100 °C, 5807 cm^{-1} at 150 °C, and 5808 cm^{-1} at 200 °C and 250 °C.

	$B_\mathrm{T}(6300-\bar{\nu}(\max))/\mathrm{km \cdot mol^{-1}}$					
	30 °C	50 °C	100 °C	150 °C	200 °C	250 °C
50 bar	0.681	0.680	0.684	0.686	0.686	0.694
500 bar	0.692	0.690	0.692	0.691	0.688	0.692
1000 bar	0.704	0.704	0.704	0.705	0.702	0.704
1500 bar	0.716	0.717	0.716	0.718	0.712	0.715
2000 bar	0.719	0.711	0.732	0.728	0.722	–

The independence of $B(6300-\bar{\nu}(\max))$ on temperature and density, which is derived from the experimental intensity data along isobars (Table 1), is of general importance for the calibration of optical layers in high-pressure high-temperature cells.

From the $\Delta l(P)$-values, final integrated molar absorptivities $B(6300-\bar{\nu}(\max))$ and total band intensities $B(6300-5060)$ are calculated (Table 2). The correction terms $\Delta l(T)$ and $\Delta l(P)$ are sufficient to yield a constant value of $B(6300-\bar{\nu}(\max))$ throughout the experimental temperature and pressure range. The mean value turns out to be:

$$B(6300-\bar{\nu}(\max)) = 0.680 \pm 0.005\ \mathrm{km \cdot mol^{-1}}\,.$$

Another way of expressing this result is by saying that Lambert-Beer's law is valid for the high-frequency half-band of the n-heptane combination mode $\nu_\mathrm{a} + \nu_\mathrm{s}$ within an extended pressure and temperature regime.

Table 2. Integrated molar absorptivities $B(6300-\bar{\nu}(\max))$ and $B(6300-5060)$ in the near infrared spectrum of pure n-heptane. $\bar{\nu}(\max)$ is the wavenumber of the absorption maximum (assigned to the $\nu_a + \nu_s$ combination mode). T, P, ϱ, and l are the experimental temperature, pressure, n-heptane density, and optical path length, respectively.

T °C	P bar	ϱ g · cm^{-3}	l µm	$B(6300-\bar{\nu}(\max))$ km · mol^{-1}	$B(6300-5060)$ km · mol^{-1}
30	50	0.680	1883	0.680	2.249
	500	0.714	1912	0.680	2.206
	1000	0.741	1944	0.681	2.168
	1500	0.761	1976	0.681	2.128
	2000	0.778	2008	0.673	2.066
50	50	0.664	1885	0.679	2.266
	500	0.702	1914	0.679	2.225
	1000	0.730	1946	0.681	2.187
	1500	0.752	1978	0.682	2.152
	2000	0.770	2010	0.666	2.074
100	50	0.622	1889	0.683	2.301
	500	0.672	1918	0.681	2.251
	1000	0.705	1950	0.681	2.201
	1500	0.730	1982	0.681	2.168
	2000	0.749	2014	0.686	2.143
150	50	0.574	1894	0.685	2.340
	500	0.642	1923	0.680	2.279
	1000	0.681	1955	0.682	2.241
	1500	0.709	1987	0.683	2.204
	2000	0.731	2019	0.682	2.176
200	50	0.517	1898	0.685	2.369
	500	0.613	1927	0.677	2.299
	1000	0.659	1959	0.679	2.267
	1500	0.690	1991	0.678	2.224
	2000	0.714	2023	0.676	2.225
250	50	0.450	1904	0.693	2.399
	500	0.585	1933	0.681	2.331
	1000	0.636	1965	0.681	2.288
	1500	0.671	1997	0.681	2.249

It should be noted that uncertainties in the determination of I_0 and in the position of the base-line for integration, are not included in the standard deviation. Both effects, which may introduce an additional uncertainty of ± 2% are, however, of the same magnitude for the whole set of data in Table 2. Recently, Borschel and Vögele [9] remeasured the near infrared absorption of pure n-heptane on a grating instrument (CARY 17 DHI). In nice agreement with the present investigation, they determined the high wavenumber half-band intensity to be:

$$B(6250-\bar{\nu}(\max)) = 0.676 \pm 0.005\ \mathrm{km \cdot mol^{-1}}.$$

The integrated molar absorptivity for the total near infrared absorption in Fig. 2, $B(6300-5060)$, is plotted versus the n-heptane density in Figure 4. The experimental data measured between 30 °C and 250 °C up to pressures of 2 kbar closely fit to a single curve. The integrated intensity is independent of temperature. With increasing density, $B(6300-5060)$ is lowered. The effect is relatively small but occurs well beyond the limits of experimental accuracy. As the half-band intensity $B(6300-\bar{\nu}(\max))$ turned out to be independent of density (Table 2), it seems reasonable to assume that also the total band integrated molar absorptivity of the $\nu_a + \nu_s$ combination mode remains constant within an extended region of states. The density dependence of $B(6300-5060)$, which is the intensity of both vibrations, $\nu_a + \nu_s$ and $2\nu_a$, indicates that the integrated intensity of $2\nu_a$ decreases with density.

A very similar type of behaviour has been found for the integrated molar absorptivities of the ν_9 and ν_{11} fundamentals in pure ethylene: The absorption intensity of both vibrations is independent of temperature. In addition, ν_{11} is independent of density

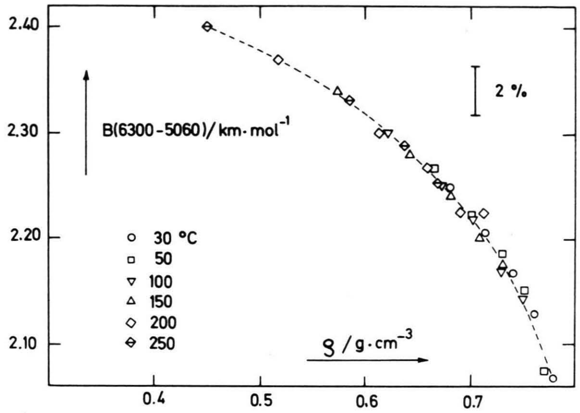

Fig. 4. Density dependence of the integrated molar absorptivity $B(6300-5060)/\mathrm{km \cdot mol^{-1}}$ of pure n-heptane in the temperature range from 30 °C to 250 °C.

while the ν_9 intensity slightly decreases toward high densities. A plot of the sum of the intensities of the slightly overlapping bands, $B(\nu_9) + B(\nu_{11})$, versus density has the same appearance as the n-heptane data in Figure 4. Two conclusions are derived from this comparison: (i) The close agreement of the results for the two non-polar materials provides strong and independent evidence for the quality of the correction terms $\Delta l(P)$ and $\Delta l(T)$ derived and used within this paper. Other numbers for $\Delta l(P)$ and $\Delta l(T)$ would fail to represent the $B(6300-5060)$ data by a single curve as in Figure 4. (ii) The integrated molar absorptivity of C–H stretching vibrations in non-polar materials is independent of temperature and is only slightly dependent and for some vibrations even independent of density.

The decrease of the integrated intensity observed toward high densities is in remarkable contrast to the situation observed in the infrared spectrum of the O–H, the N–H, and the H–Cl stretching fundamentals in pure water [10], pure ammonia [11], and pure hydrogen chloride [12], respectively. Increasing density at constant supercritical temperature raises the integrated intensities between gaseous and liquidlike densities by about a factor of three. Whereas these large effects are due to strong attractive interactions, the small variations and especially the decreasing C–H vibrational intensity observed toward dense states are attributed to the importance of repulsive interactions which come into play at the highest fluid densities in n-heptane (Fig. 4) and in ethylene [3]. Unfortunately, the theory of integrated intensities in dense fluids is only poorly developed at present. The good quality of the experimental data and the striking differences observed in the infrared spectra of polar and non-polar materials may, however, stimulate theoretical efforts to provide a basis for the discussion in quantitative terms.

With respect to quantitative analysis at high pressures and temperatures two conclusions are derived from the n-heptane spectra: (i) The equipment for optical high-pressure work is well developed and, for layers of millimeter size, enables absorption intensities to be measured with good precision of better than $\pm 1\%$. (ii) Vibrational modes ν_i exist with integrated molar absorptivities $B(\nu_i)$ being independent of temperature and density within an extended region of states. Vibrations of this type offer important applications for quantitative kinetic and thermodynamic studies on pressurized systems as their absorbances are strictly proportional to density.

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