Infrared Spectrum of Pure Fluid Carbon Monoxide

M. Buback, J. Schweer, and H. Tups
Institut für Physikalische Chemie der Universität Göttingen

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The infrared fundamental of pure CO is measured at supercritical temperatures between 298 K and 450 K up to a maximum pressure of 267 bar. The experimental IR bandshapes are adequately represented by summing up over the individual lines of the gaseous rotation-vibration spectrum assuming half-widths to be proportional to density. The molar integrated absorptivity is found to be independent of temperature and density which enables direct and precise measurements of CO concentrations in fluid phase equilibria and reactions.

Introduction

High-pressure high-temperature vibrational spectroscopy provides information on the structure and dynamics in fluids. Experiments at supercritical temperature are especially interesting as spectra may be recorded at continuous density variation between gaseous and liquid-like states. In polar materials, such as water [1], hydrogen chloride [2], and ammonia [3] infrared band shape, band position, and vibrational intensity turned out to strongly depend on pressure and temperature. With the availability of high-performance Fourier-transform spectrometers and using refined high-pressure experimental techniques, the precise measurement even of the small pressure and temperature effects which are typical for less polar and unpolar materials, is within reach. In the limiting situation of vibrational intensities being independent of P and T, infrared spectroscopy offers the important advantage of direct and precise measurement of concentrations in high-pressure high-temperature kinetic and thermodynamic experiments. The infrared and near infrared spectra of pure fluid ethene [4–6] have already been investigated and quantitative vibrational spectroscopy has been extensively applied to the study of the high-pressure ethene polymerization [7]. Carbon monoxide is another interesting material. The diatomic molecule is only slightly polar which facilitates interpretation of the fluid state absorption spectra. Moreover, due to the enormous technical importance of carbon monoxide reactions in the compressed gaseous state [8], all aspects of direct analysis of CO concentrations under pressure via IR spectroscopy are of interest. The first and second overtone absorption spectra of CO have already been investigated between 293 K and 500 K and up to 2.8 kbar [9]. Band shape, maximum position, and vibrational intensity are studied as a function of density and temperature. With respect to analytical applications, it turned out that CO concentrations in the fluid state may be derived from overtone absorption bands within an accuracy of a few per cent. Because of the lower molar absorptivity of overtones, the method is, however, less accurate at small CO concentrations where, for quantitative purposes, the absorption of the intense CO fundamental mode should be used. The aim of the present paper is to measure the CO fundamental to elevated pressures and temperatures. Due to the strong absorptivity of the 0 → 1 vibrational transition [10], in studies on compressed CO, optical path lengths well below one millimeter have to be used. The maximum CO density is chosen to be 0.175 g $\cdot$ cm^{-3} which enables spectroscopic experiments to be performed at path lengths of the order of 0.1 mm. They are sufficiently large as to be corrected for their pressure and temperature dependence if P and T are below 300 bar and 500 K, respectively.

The fundamental mode in gaseous CO has already been extensively studied by theoretical methods [11–17] and by infrared and Raman techniques [10, 18–23]. Spectroscopic investigations in the compressed fluid, in the liquid, and in the solid state have only been performed at or below room temperature [20–23]. Within the present paper, the infrared spectrum of fluid CO is investigated between 298 K and 450 K. The highest CO density of 0.175 g $\cdot$ cm^{-3}, at 450 K corresponds to a maximum pressure of 267 bar.

Reprint requests to Prof. Dr. M. Buback, Institut für Physikal. Chemie der Universität Göttingen, Tammannstraße 6, D-3400 Göttingen.

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Experimental

The experimental set-up and the optical cell of transmission type with two sapphire windows are described elsewhere [24, 25]. The stainless steel cell is heated electrically from outside. Temperatures and pressures are measured within ± 0.5 K and ± 2 bar, respectively. The optical path length at ambient temperature and pressure was $l_0 = 0.079$ mm. The variation of the optical path length with P and T, which for the highest pressures and temperatures reaches almost fifty per cent of l_0, via linear correction terms as obtained from careful calibration work [25], may be calculated such that the remaining uncertainty in optical path length is below ± 2.5%. Spectra are recorded on a Fourier transform interferometer (Bruker IFS 45) with 1 cm^{-1} resolution. The decadic absorbance A as a function of the wavenumber $\bar{\nu}$ is converted into molar absorptivity ε:

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

where c and l are the actual values of CO concentration (or CO density) and optical path length, respectively. The CO density is obtained within ± 1% from the published equation of state [26, 27]. Integration over the total infrared band yields the integrated molar absorptivity (or vibrational intensity) B:

$$B = \int \varepsilon(\bar{\nu}) \cdot \mathrm{d}\bar{\nu}\,. \qquad (2)$$

Due to several sources of uncertainty, the accuracy of the experimental B-values can be as large as ± 4%.

Results

The molar absorptivity ε of the fundamental mode in pure CO is plotted for several densities at 400 K in Figure 1. The ε-curves are shifted in the baseline in order to avoid strong intersection. The pressures corresponding to the spectra at 0.050 g $\cdot\,\text{cm}^{-3}$ and 0.150 g $\cdot\,\text{cm}^{-3}$ CO density are 60 bar and 193 bar, respectively. The absorption contour is essentially determined by the envelope of the gaseous P- and R-branches. Pressure-broadened individual rotation-vibrational lines are weakly indicated in the P-branch of the lowest density spectrum (0.050 g $\cdot\,\text{cm}^{-3}$). The minimum between the P- and R-branches becomes less pronounced toward higher density (Figure 1).

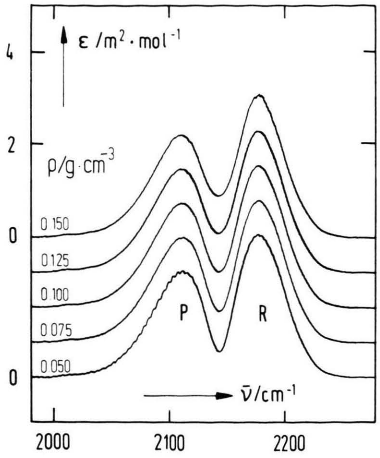

Fig. 1. Molar absorptivity ε of the stretching fundamental in pure carbon monoxide at 400 K for several densities between 0.05 g $\cdot\,\text{cm}^{-3}$ and 0.15 g $\cdot\,\text{cm}^{-3}$.

Discussion

High-pressure vibrational spectroscopy at supercritical temperature enables compressed fluid states, by a sequence of spectra measured at arbitrary intermediate densities, to be connected with the dilute gaseous state which, in general, is spectroscopically well understood. Spectra measured at gradually increasing pressure may indicate whether parameters of the gaseous spectrum provide a reasonable representation of spectra at slight or even moderately high compression.

With respect to the density dependence of vibrational band shape, Bouanich et al. [28, 29] developed a model for the description of the normalized molar absorptivity band contour, $\varepsilon_n(\bar{\nu}) = \varepsilon(\bar{\nu})/B$, where B is the vibrational intensity of the corresponding fundamental or overtone mode. The model, which has already been tested in the first and second overtone region [9, 28, 29], is essentially based on parameters known from the gaseous spectrum. The band profile is generated by summing over the individual rotation-vibration lines, which are assumed to have half-widths proportional to density. A single adjustable parameter α modifies the individual line profile from a Lorentzian ($\alpha = 0$) to an almost Gaussian shape at $\alpha = 1$. The expression for the normalized band contour of the fundamental mode is

$$\varepsilon_n(\bar{\nu}) = \frac{\sum\limits_m \exp\left(\frac{-E_{\mathrm{rot}}(m)}{k\cdot T}\right)\cdot F(m)\cdot |m|\cdot \exp\left(-\alpha\left(\frac{\bar{\nu}-\bar{\nu}(m)}{K(|m|)}\right)^2\right)\cdot \frac{K(|m|)}{K(|m|)^2+(\bar{\nu}-\bar{\nu}(m))^2}}{C(\alpha)\cdot \sum\limits_m \exp\left(\frac{-E_{\mathrm{rot}}(m)}{k\cdot T}\right)\cdot F(m)\cdot |m|} \qquad (3)$$

m is the summation index which characterizes the rotation-vibration line. Actually, values from $m = -30$ up to $m = +31$ have been considered. $E_{\mathrm{rot}}(m)$ is the rotational energy of the initial state. The vibration-rotation coupling function $F(m)$ is expressed as a quadratic polynomial with the two Herman-Wallis coefficients taken from literature [17]. The line positions $\bar{\nu}(m)$ are gas-phase literature data [30]. $K(|m|)$ is defined as

$$K(|m|) = \gamma_0(|m|)\cdot\frac{1+2\alpha}{1+\alpha}\cdot\frac{\varrho}{\varrho_0}, \qquad (4)$$

where $\gamma_0(|m|)$ is the known half-width at the reference gas density ϱ_0 (298.15 K, 1.013 bar) [28] and ϱ is the experimental density at pressure P and temperature T. $C(\alpha)$ in (3) is the normalization factor.

A comparison of experimental and calculated ((3) and (4) with $\alpha = 1$) spectra for 0.1 g · cm^{-3} CO density at 298 K and 450 K is illustrated in Figure 2. With the exception of small deviations in the vicinity of the absorption minimum between the P- and R-branches, both data sets are in good agreement. The remarkable result from Fig. 2 is that, with a single adjustable parameter, the broad band contour of fluid CO at least up to 142 bar (0.1 g · cm^{-3} at 450 K) is obtained by summing up rotation-vibration lines with half-widths being assumed to increase linearly with density. Fair agreement of experimental and theoretical curves is also observed for 0.15 g · cm^{-3} density. Corresponding analysis of the first and second overtone spectra showed that fluid state spectra may be adequately calculated from gaseous rotation-vibration lines almost up to the critical density (0.301 g · cm^{-3}) [9].

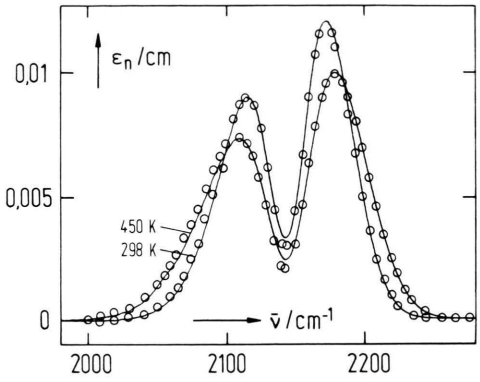

Fig. 2. Comparison of experimental (——) and calculated (○) bandshapes for the fundamental mode of pure CO at 0.1 g · cm^{-3} density for 298 K and 450 K.

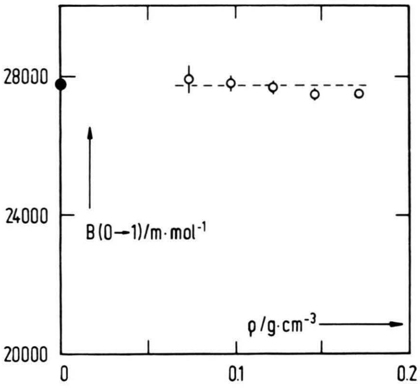

Fig. 3. Integrated molar absorptivity $B\,(0 \rightarrow 1)$ of pure CO plotted versus density at temperatures between 350 K and 450 K. The gaseous vibrational intensity (●) is from Ref. [10].

With respect to quantitative analysis, the density and temperature dependence of the vibrational intensity is of primary importance. B is plotted versus density in Figure 3. A variation of the vibrational intensity with temperature is not observed. Each of the data points in Fig. 3 is the arithmetic mean of experiments between 350 K and 450 K. The very weak decrease of B toward higher density, which is suggested by the data, is too small as to be safely established. It should, however, be noted that the vibrational intensities of the first and second overtone decrease by a few per cent between gaseous and liquid-like densities up to about 0.7 g · cm^{-3} [31]. Within the limits of experimental error being essentially determined by the imprecise knowledge of the actual optical path length, B is found to be constant within the pressure and temperature range under investigation: $B(0 \rightarrow 1) = 27\,700 \pm 350\ \mathrm{m \cdot mol^{-1}}$. This value is in very good agreement with the literature value of the gaseous CO vibrational intensity: ($B_{\mathrm{gas}}(0 \rightarrow 1) = 27\,820\ \mathrm{m \cdot mol^{-1}}$) [10].

A constant value of B at known optical path length, according to (1) and (2), enables the calculation of CO concentrations from measured absorbance spectra. As, in addition, the overtone vibrational intensities are well suited for quantitative purposes ($B(0 \rightarrow 2)$ decreases by 0.3 per cent for a $0.1\ \mathrm{g \cdot cm^{-1}}$ increase of the CO density and is independent of temperature between 293 K and 500 K. $B(0 \rightarrow 3)$ decreases by 1.0 per cent for a $0.1\ \mathrm{g \cdot cm^{-3}}$ density increase and is also insensitive to temperature change), several vibrational modes are available for the study of CO concentrations in kinetic and in thermodynamic experiments at high pressures and temperatures. The fundamental as well as first and second overtone spectra of carbon monoxide at $0.15\ \mathrm{g \cdot cm^{-3}}$ and 400 K are presented on a logarithmic molar absorptivity scale in Figure 4. There are at least two possibilities to take advantage of ε changing by several orders of magnitude between the fundamental and the second overtone modes: (i) If, e.g. in process control, a CO concentration of about $0.15\ \mathrm{g \cdot cm^{-3}}$ is to be measured, quite different path lengths and thus reactor dimensions can be used. To ensure reasonable optical quality of the spectra, the absorbance in the maximum should not exceed $A_{\max} = 1$. Thus from the $\varepsilon_{\max}$-values in Fig. 4 the maximum optical path lengths are calculated to be 0.066 mm, 7.9 mm, and 1120 mm in the fundamental, first, and second overtone regions, respectively. Via (1) the corresponding path lengths for any other fluid CO density are calculated. (ii) Within kinetic experiments, concentrations may vary by orders of magnitude. As the wavenumber range in Fig. 4 can be simultaneously recorded on modern Fourier transform interferometers, the large changes in molar absorptivity enable quite different concentrations to be measured with comparable sensitivity within one experimental run: Starting materials are studied via overtone spectroscopy and the first traces of products are measured in the fundamental range. If high conversions are reached, the appreciable product concentrations are recorded in the overtone region and remaining small quantities of starting material are identified via the fundamental mode. With respect to CO, from the ε-values in Fig. 4 and for an arbitrarily chosen path length of 250 mm, an absorbance of $A_{\max} = 1$ in the band maximum corresponds to CO concentrations of $3.9 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$, $4.7 \cdot 10^{-3}\ \mathrm{g \cdot cm^{-3}}$, and $0.67\ \mathrm{g \cdot cm^{-3}}$ in the fundamental, first, and second overtone mode, respectively. It should be noted that in order to apply quantitative vibrational spectroscopy along these lines, no serious band overlap with other vibrational components should exist.

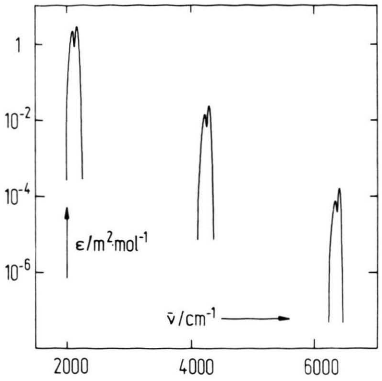

Fig. 4. Molar absorptivity ε of pure carbon monoxide at 400 K and 193 bar ($\varrho = 0.15\ \mathrm{g \cdot cm^{-3}}$) in the mid- and near-infrared region from $1500\ \mathrm{cm^{-1}}$ to $7000\ \mathrm{cm^{-1}}$.

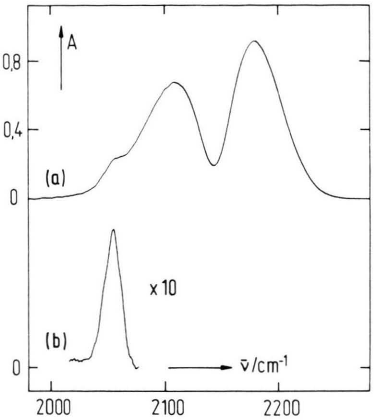

Fig. 5. (a): Infrared absorbance measured on fluid CO (450 K, 105 bar) contained in a stainless steel cell (optical path length 0.109 mm). (b): Difference spectrum (multiplied by a factor of 10) between (a) and the absorbance spectrum of pure CO at identical temperature and pressure (see text).

Quantitative high-pressure spectroscopy on carbon monoxide has already been used in kinetic studies on the copolymerization of ethene and CO at pressures and temperatures up to 2900 bar and 513 K, respectively [32, 33]. Further applications of the method are to be expected in the extended field of reactions starting from $CO-H_2$-mixtures at elevated pressure [34]. The direct study of metal carbonyls under pressure and in the presence of large amounts of CO is also feasible, as is illustrated in Figure 5. The spectrum in the upper part of Fig. 5 is measured on carbon monoxide contained in a stainless steel cell at 450 K and 105 bar. The cell material (RGT 601, W.-Nr. 2.4668) consists to more than fifty per cent of nickel. The formation of $Ni(CO)_4$ is identified by subtracting the pure CO spectrum (of identical density) from the experimental curve. This procedure, as is shown in the lower part of Fig. 5, yields the carbonyl absorption [35, 36]. Along these lines the kinetics of carbonyl formation and the stability of these species may be studied within an extended pressure and temperature range.

The results of the present paper may be summarized: the IR fundamental absorption in fluid CO, at least up to moderate compression, is closely related to the gaseous spectrum. The validity of Lambert-Beer's law enables direct quantitative analysis of CO. The method is of special importance if the fundamental as well as the first and second overtone absorption are simultaneously recorded, which allows to measure CO up to high pressures and temperatures in systems which appreciably vary in size and in carbon monoxide concentration.

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