Anomalous Behaviour of the Mean Dipole Polarizability α of Neopentane $C(CH_3)_4$ in the Temperature Range between 250 K and 360 K

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The temperature dependence of the dynamic dipole polarizability $\alpha(\lambda)$ of gaseous neopentane has been re-examined in the temperature range between $T = 250$ K and $T = 360$ K at the four HeNe-laser wavelengths $\lambda = 543.51$ nm, 594.11 nm, 611.97 nm, and 632.99 nm. These interferometric measurements are compared with former determinations of the dynamic as well as the static dipole polarizability in the solid, liquid and gaseous state. In all cases, a shape of $\alpha(T)$ in the range between 290 K and 310 K has been observed which is similar to the shape of $\alpha(\lambda)$ in an absorption band. This observation is connected with other physico-chemical quantities of neopentane.

Key words: Thermal excitation, Refractive index, Polarizability, Gases, Neopentane

1. Introduction

The globular molecule neopentane $C(CH_3)_4$ has experienced considerable interest in the past. Because of its high symmetry, spectroscopists are interested in the IR- and Raman active modes (see e.g. [1–9]) as well as in the description of the torsional motions of the methyl-groups [10], which are also well examined by scattering of cold neutrons [11]. The thermodynamic interest in this molecule is also due to its highly symmetric and globular structure. Therefore, there exist careful investigations of the thermodynamic properties, too (see e.g. [12–17]). In all these experiments, at first sight, no anomalous behaviour of the physico-chemical quantities of $C(CH_3)_4$ has been detected. However, in experiments concerning the temperature dependence of the polarizability α of neopentane, anomalous behaviour seems to occur in the range between $T = 290$ K and $T = 310$ K. This has been first stated by Ashton et al. [18], who have measured the refractivity of gaseous $C(CH_3)_4$ with a Jamin-type interferometer and stated that "the value of P^0 [= molar refraction, proportional to α] at 40 °C differs from the values at the other temperatures by an amount considerably greater than the experimental scatter and we have found no explanation for this". In the following, Kerl et al. [19–22] have observed a minimum in the dynamic polarizability $\alpha(\lambda)$ of the free molecule in the vicinity of $T = 300$ K by precise measurements of the refractive index using a modified Michelson-interferometer. Additionally, measurements of the dielectric constant ε of solid $C(CH_3)_4$ under high pressure [23] as well as the determination of ε in the liquid state [24] have shown that the static polarizability $\alpha(\lambda \to \infty)$ also reaches a minimum value in the vicinity of $T = 300$ K.

Being now in possession of a new Michelson-twin interferometer, whose geometry is optimized for the determination of the temperature dependence of the polarizability of gaseous species, as has been already shown in detail [25–29], we felt that the effect is worth a careful re-examination. We believe that the results presented in this work are superior to those formerly determined in our laboratory (see [19–22]) on account of the very stable interferometric device as well as the better construction of the gas sample cell used [25].

2. Theoretical

The origin of the temperature dependence of the electron polarizability α of small non-polar molecules is already discussed elsewhere [26]. To summarize it in a simple manner, we will refer to the early treatment of Bell [30]. He associates an increase in α with rising

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temperature T of diatomics with an increase in the mean internuclear distance on account of the occupation of higher rotational and vibrational molecular levels. This leads to the simple approximation

$$\alpha(T)-\alpha(T_0)=\frac{\partial\alpha}{\partial r}\,[\bar{r}(T)-\bar{r}(T_0)]\,, \tag{1}$$

where $\partial\alpha/\partial r$ is the change of α with the internuclear distance r, e.g. well-known from Raman spectroscopic experiments; $\bar{r}(T)$ is the mean internuclear distance at temperature T. This simple formula may be somewhat improved by introducing spectroscopically measurable quantities and by considering higher derivatives of α, as was done by Buckingham [31]. It has been shown that our latest experimental results concerning diatomics as well as methane can be described quite well by relations like (1) in the temperature-range between 300 K and 1100 K [26]. In all cases a smooth continuous rise of α with increasing temperature was observed experimentally in the order of 1%/ 1000 K, which is also predicted by (1).

Even in the case of diatomics, an exact theoretical treatment of the temperature dependence of the polarizability is extremely difficult [32], and only in the case of H_2 highly accurate ab initio calculations of the temperature dependence of the dynamic polarizability $\alpha(\lambda)$ exist, which, however, fit very nicely to our experimental results [33].

Nevertheless, up to now only a very crude treatment of the T-dependence of α of $C(CH_3)_4$ was given by us [19] using Bell's simple picture of $\alpha(T)$ of diatomic molecules [30]. Therefore, in this treatment only a monotonical increase of α with rising temperature is predicted; there should be no minimum in the polarizability at moderate temperatures.

3. Experimental

The equipment [25] as well as the experimental procedure used to determine $\alpha(\lambda, T)$ are described in full detail elsewhere [29]. The main procedure is the simultaneous isothermal determination of the pressure- and wavelength-dependence of the refractive index $n(\lambda, T, p)$ of gaseous $C(CH_3)_4$ in the range $p \leq 0.7\,p_{\mathrm{sat}}(T)$ ($p_{\mathrm{sat}}(T)$ = vapour pressure at T), using the four HeNe-laser wavelengths 632.99 nm, 611.97 nm, 594.11 nm and 543.51 nm simultaneously. The temperature range investigated is between 250 K and 360 K, with special interest in the interval between 285 K and 300 K. The measured refractive index n is fitted to a modified Lorentz-Lorenz equation, which is written in terms of the ideal gas-density $\varrho_0 = p/RT$ in the following manner [29]:

$$\frac{n^2(\lambda, T, p)-1}{n^2(\lambda, T, p)+2}\,\frac{1}{\varrho_0}=A_1(\lambda, T)+A_2(\lambda, T)\,\varrho_0\,. \tag{2}$$

A_1 and A_2 are connected with the mean dipole polarizability α of the non-interacting particle, the second refractivity virial coefficient b_R and the second thermodynamic virial coefficient B via

$$A_1(\lambda, T)=\tfrac{4}{3}\pi N_A\,\alpha(\lambda, T), \tag{3}$$

$$A_2(\lambda, T)/A_1(\lambda, T)=b_R(\lambda, T)-B(T)\approx -B(T)\,. \tag{4}$$

N_A is the Avogadro constant.

The purity of the neopentane used was better than 99%, the main impurity being n-butane. We have used two different gaseous specimens (Linde AG, Germany, and Matheson Co., USA), but no systematic differences have been detected in the measured polarizabilities $\alpha(\lambda, T)$ determined with (3).

4. Results and Discussion

In Fig. 1 the experimental results $\alpha(\lambda, T)$ of this work (crosses, open squares) are compared with other available data. Generally, the error bars are smaller than the points shown. At first sight a comparison and interpretation of the data shown in Fig. 1 may be difficult on account of the large scattering and deviations of the data points. But a closer look will soon show some similarities between all measurements.

a) The data of this work are determined at four wavelengths, given in § 3. Due to the high accuracy of the measured dispersion of the polarizability, we have also extrapolated our data to the static limit $\alpha(\lambda\to\infty)$, using the well-known Cauchy-relation $\alpha(\lambda)=a+b/\lambda^2$ ($a(T)$ and $b(T)$ have been determined for each T). For the sake of clarity, in Fig. 1 we have only shown the polarizabilities determined at 632.99 nm (crosses, 73 data points, error bars smaller than the symbols used) and the extrapolated static ones (open squares, again 73 data points, error bars in the order of the height of the symbols). In general, a very smooth increase of α with rising temperature was determined, and both data sets nearly show the same temperature dependence. But in the vicinity of $T = 295$ K the shape looks like the polarizability curve $\alpha(\lambda)$ determined in

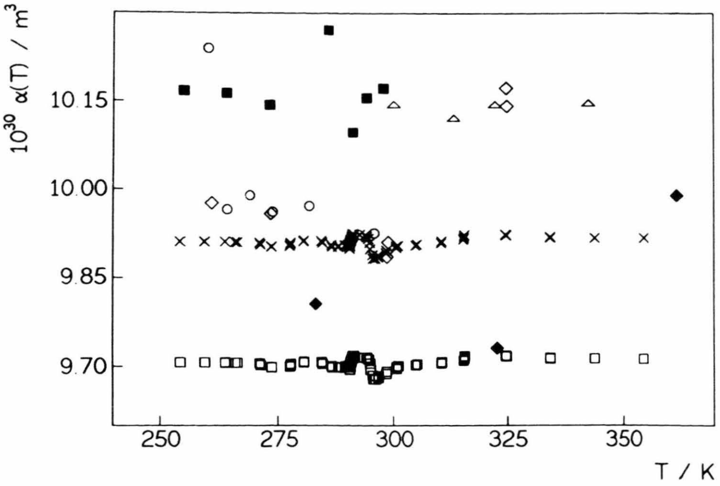

Fig. 1. Measured polarizabilities $\alpha(T)$ of neopentane in the gaseous state (□ $\lambda \to \infty$, × $\lambda = 632.99$ nm, both this work; △ [18], ◆ [20], ◇ [21], all $\lambda = 546.226$ nm), liquid state (○ [24], $\lambda \to \infty$), and solid state (■ [23], $\lambda \to \infty$).

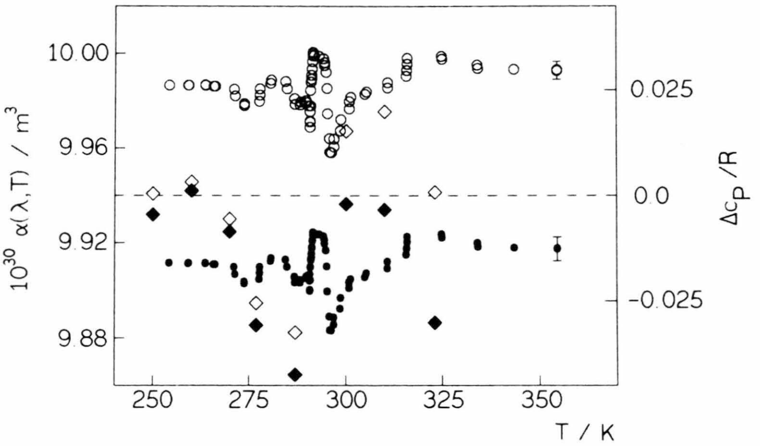

Fig. 2. Measured polarizabilities $\alpha(\lambda, T)$ (left scale, ● $\lambda = 632.99$ nm, ○ $\lambda = 543.51$ nm, this work; mean standard deviation of the data shown at $T = 355$ K), and deviations Δc_p (right scale) of measured ideal gas-state heat capacities c_p [17] from calculated data ◆ and fitting-curve data ◇ ([17], (36)).

an absorption band (see e.g. [34]). There is a sharp rise, followed by a fast decrease, and again a slow increase of α with increasing temperature. In Fig. 2 the polarizabilities determined at 632.99 nm (open circles) and 543.51 nm (full circles) are shown in greater detail, together with measured data of the molar heat capacity c_p of neopentane (see below).

b) The earlier measurements performed in our laboratory using a different Michelson interferometer are indicated in Fig. 1 by full rhombi [20] (3 points) and by open rhombi [21] (6 points). They are all determined at $\lambda = 546.226$ nm. The full rhombi [20] are widely spaced, showing their minimum value near $T = 320$ K. Due to these few points, the fine structure of the T-dependence of α is not detectable. In contrast to this, the open rhombi [21] are closer spaced, and obviously there is a minimum of α in the vicinity of $T = 300$ K, which was confirmed by two independent measurements at nearly the same temperature. Both data sets are determined with the same equipment. The data given in [22], which also show a large gap at $T = 295$ K, are not shown because we felt that a systematic error has occurred during the measurements just between $T = 280$ K and $T = 310$ K.

c) The early gas-phase measurements of Ashton et al. [18] at $\lambda = 546.226$ nm are indicated in Fig. 1 by open triangles (4 points). As mentioned in the introduction they obviously show a minimum in the vicinity of $T = 310$ K. But unfortunately no measurements were carried out below 300 K.

d) The static polarizabilities in the solid state at 500 atmospheres (full squares, 7 points) are gained using data of the dielectric constant ε and density ϱ, which are connected via the Clausius-Mossotti equation [23]. The measured polarizabilities are relatively large, which may be characteristic for the solid state. But nevertheless, the s-shaped curve, inherent in the data of this work at $T=295$ K, may be recognized in these data, too. There is a sharp rise at $T=286$ K, followed by a decrease at $T=292$ K and then again a slow increase. This statement, however, has to be considered with great care, on account of the few data given in [23], which are not spaced close enough in the T-range we are interested in.

e) Finally, the circles indicate the static polarizabilities measured in the liquid state (6 points), again using ε and ϱ values combined with the Clausius-Massotti equation [24]. The few data available show their minimum value at $T=296$ K.

Considering all these experimental results, we believe that in the vicinity of $T=295$ K (or at least in the larger range between $T=285$ K and $T=310$ K) an anomalous behaviour of α of $C(CH_3)_4$ exists, in the sense that there must be a sudden change of α with temperature. We now have to discuss possible origins of this unusual effect, which we have not observed in the case of neat n-butane, which is the main impurity in the neopentane sample used in this work. Because the effect considered is observed in both, the ideal gas phase as well as in the condensed phases, its origin should be caused by intramolecular motions. Using Bell's simple model [30], an abrupt change in α can only be caused by a sudden change in the mean internuclear distance. However, this can only be achieved by a more or less sudden occupation of vibrational and rotational levels of the molecule. Selective excitation of higher molecular energetic levels is normally achieved by the use of photons of appropriate energy $E=\hbar\omega$ and not by the use of thermal energy $E=kT$, which usually is distributed over the whole molecule. Nevertheless, one possible temperature effect has to be a change in the molar heat capacity c_P of $C(CH_3)_4$, which is closely related to all rotational and vibrational energies of the molecule, as is known from standard textbooks in statistical mechanics (see e.g. [35], §§ 46–51). Obviously, the only data of c_P in the temperature range given above are determined by measurements of the speed of sound in gaseous neopentane in the range between 250 K and 323 K by Ewing et al. [16, 17]. These are in excellent agreement with the flow calorimetric measurements of Hossenlopp et al. [15] in the range between 298 K and 523 K. At first sight, both data sets show a very monotonic increase of c_P with rising temperature. To see possible irregularities, we have calculated the heat capacities, using the available experimentally determined frequencies of the normal modes of vibration [4, 7], together with the given frequencies of the torsional modes of the methyl groups [10]. But in the latter case we have interchanged the frequencies of the a_2 and f_1 modes given by Durig et al. [10], because otherwise only very poor agreement between the calculated and the measured data can be achieved. With the assumption of harmonic oscillation as well as fully excited rotational motion of the whole molecule we have calculated c_P according to well-known formulae (see [35], § 51), and the difference $\Delta c_P = c_P(\text{calc.}) - c_P(\text{meas. [17]})$ is shown in Fig. 2 (full rhombi). The agreement is generally in the order of 0.05% with the exception in the vicinity of $T=290$ K where a much larger deviation can be seen. This was already described by Ewing et al. [17], who have fitted their experimental results to an empirical formula ((36) in [17]). The deviations between the fit and the experimental results (see Fig. 2, open rhombi) show a jump of $\Delta c_P/R \approx 0.05$ at $T=295$ K, which is larger than the stated accuracy of the measurements of $\delta c_P/R = 0.015$. Ewing et al. [17] attributed this jump to a possible impurity in their substances.

Sudden changes in c_P are well-known and are generally connected with phase transitions or transitions of hindered into free intramolecular rotation, respectively. The changes in c_P associated with these two effects are usually much larger than 0.05 R. Nevertheless, the thermal energy at $T=295$ K can be associated with a wavenumber of $\sigma = kT/hc = 205\ \text{cm}^{-1}$. It is remarkable, that this wavenumber is comparable to that of the lowest torsional mode measured to be $221\ \text{cm}^{-1}$ in the solid state [10]. Perhaps this indicates that near 295 K neopentane exhibits an "intramolecular phase transition", which means a collective phenomenon concerning the sudden occupation of higher torsional eigenstates of the methyl-groups of the $C(CH_3)_4$-molecule, which possesses a torsional barrier of nearly $1500\ \text{cm}^{-1}$. A somewhat similar statement has been given by Kerl [20], who associates the temperature at which the change in α occurs with the wavenumber of intramolecular motions of $C(CH_3)_4$.

A rigorous theoretical treatment has shown that the nuclear electromagnetic shielding, which determines the resonance frequency in NMR-spectroscopy, is strongly related to the polarizability of a molecule (see [36] and references therein). Therefore, temperature dependent measurements of the carbon-13 NMR shift of $C(CH_3)_4$ possibly should show the same unexpected behaviour as the polarizability itself. Unfortunately, highly accurate measurements concerning the T-dependence of the shift are very difficult to perform, and the results given in the literature are not precise enough to recognize an abnormal temperature dependence [37].

Recently, Weiss et al. [38] have determined the linewidth $\Delta B(^1H)$ and the second moment $M_2(^1H)$ of the NMR-signal of the nearly globular molecule $(CH_3)_3PbCl$ in the solid state. They observed an unexpected decrease of $\Delta B(^1H)$ and $M_2(^1H)$ in the range between 248 K and 260 K. Examination with differential thermal analysis (DTA) shows no phase transition and no explanation has been found by the authors for this unexpected effect. Perhaps, the origin is similar to that observed and discussed in the case of neopentane in this work.

So far we have considered the free non-interacting molecule. But we have to discuss effects arising from intermolecular interactions, too, which can cause an unusual behaviour in the measured polarizability. We have already observed an obvious minimum in the measured α of methane near its critical temperature at $T_C = 190.53$ K [29], which we have attributed to a collective behaviour due to intermolecular interactions. However, in the case of $C(CH_3)_4$ we believe that we are concerned with an intramolecular effect, because the observed unusual behaviour occurs in the gaseous, liquid, and in the solid state, which can be seen clearly in Figure 1.

This statement is supported by an analysis of the CH_3-deformation mode, which is nearly uneffected by the temperature in the liquid as well as the plastic crystal phases [8]. This can be explained by the globular structure of $C(CH_3)_4$, which forms a cavity, where intramolecular motions can take place rather uneffected by intermolecular interactions.

Summarizing, we have shown that an anomalous temperature dependence of the polarizability $\alpha(T)$ of neopentane in the vicinity of $T = 300$ K occurs, which can be attributed with high probability to intramolecular effects. We believe that this anomalous effect is due to the torsional motion of the methyl-groups of $C(CH_3)_4$, which possibly can cause an "intramolecular phase transition" at this temperature.

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