Infrared Studies of Rotational and Vibrational Relaxation in Liquid Cyclohexane

T. Bien and G. Döge

Institut für Physikalische Chemie, Technische Universität Braunschweig

J. Yarwood and K. E. Arnold

Department of Chemistry, University of Durham, Durham City, England

Z. Naturforsch. **37a**, 51–54 (1982); received August 28, 1981

Molecular correlation functions have been determined for the infrared active vibrations ν_{16}, ν_{29}, ν_{30} and ν_{31} of neat liquid cyclohexane at different temperatures. The results have been compared with calculated reorientational correlation functions.

1. Introduction

For the study of molecular reorientation and vibrational relaxation, infrared spectroscopy is a powerful tool. The Fourier transform (FT) of the infrared profile is the product of the vibrational and reorientational correlation functions [1]:

$$\mathrm{FT}\, I(\tilde{\nu})_{\mathrm{ir}} = \Phi_{\mathrm{vib}}(t)\, C_{\mathrm{rot}}^{1,k}(t). \qquad (1)$$

The above relationship implies that vibrational and rotational relaxation are statistically independent. When a Raman investigation of the isotropic scattering of the same band is possible (in the case of vibrations which belong to the totally symmetric species), $\Phi_{\mathrm{vib}}(t)$ is often taken from the FT of the isotropic Raman scattering and $C_{\mathrm{rot}}(t)$ may be calculated [2]. However, for molecules with a center of inversion like cyclohexane [3], the ir active vibrations are forbidden in the Raman spectrum and vice versa. Moreover, for degenerate bands there is no direct experimental way to separate the two contributions to the correlation function anyhow [4].

To overcome these difficulties, it has been proposed in recent papers to set up a model for reorientational relaxation by the aid of additional measurements (e.g. NMR-spectroscopy, vapour phase spectroscopy) and to extract the intrinsic line widths [5–7]. In this study, we report some results obtained by such methods for the parallel vibration ν_{16} (A_{2u}, at 522 cm^{-1}) and the degenerate (E_u) vibrations ν_{29} (at 1260 cm^{-1}), ν_{30} (at 906 cm^{-1}) and ν_{31} (at 862 cm^{-1}) of neat liquid cyclohexane at different temperatures. Cyclohexane was often chosen for investigations of molecular reorientation and vibrational relaxation [6, 8–13]. In a recent paper, a Raman active degenerate fundamental vibration has been studied in a similar way to that proposed here [6].

2. Experimental

Infrared measurements were made using a Perkin-Elmer model 580 B spectrometer equipped with digital readout of transmittance data. Variable temperature measurements were made with a standard CsI resp. KBr heated infrared cell and a Beckman RIIC Ltd. (TEM-1C) temperature controller. Spectral grade cyclohexane was purchased from Merck.

Molecular correlation functions were obtained from numerical fast Fourier transformation of the band contours processed on the ICL 1904 S computer at Technische Universität Braunschweig. A spectral slit width of about 1/10 of the measured half widths justifies the renunciation of deconvolution from the "slit profile". The correlation times were computed as $\tau = \int \Phi(t)\,\mathrm{d}t$. The results from multiple scans at the same temperature give an error of less than 4% of the calculated correlation times.

3. Results and Discussion

The experimental correlation times

$$\tau_{\exp} \left(= \int \mathrm{FT}\, I(\tilde{\nu})_{\mathrm{ir}}\, \mathrm{d}t\right)$$

are included in Figure 1. As expected, they differ

Reprint requests to Herrn T. Bien, Institut für Physikalische Chemie der Technischen Universität Braunschweig, 3300 Braunschweig.

0340-4811 / 82 / 0100-0051 $ 01.00/0. — Please order a reprint rather than making your own copy.

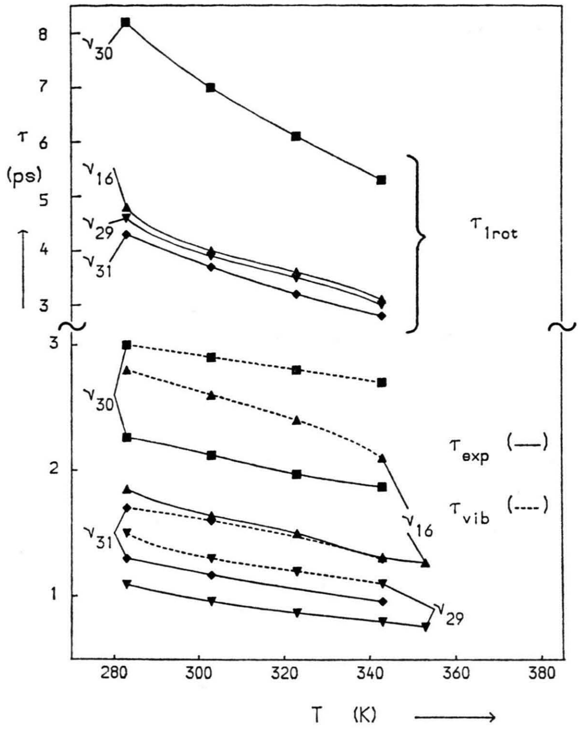

Fig. 1. Experimental and calculated reorientational and vibrational correlation times of ν_{16}, ν_{29}, ν_{30} and ν_{31} of C_6H_{12} at different temperatures.

for each fundamental vibration investigated due to different reorientational and vibrational relaxation contributions to each vibration. For vibrations where the transition moment is parallel to the symmetry axis (parallel band) the same reorientational correlation functions must be obtained, which describe an orientational motion of the main symmetry axis [14]. In the case of cyclohexane, which predominantly exists in the chair conformation (point group D_{3d} [3]), this is a C_3 axis. For a degenerate mode, the reorientational correlation functions additionally include contributions of the "spinning motion" around the main symmetry axis. The latter may be affected by Coriolis coupling so that the reorientational correlation functions may be different for each degenerate vibration [6, 7, 15].

For reorientational motion a large amount of models has been proposed so far. In this study, we assume the "Kubo model" to be valid [16]:

$$C^{1,k}_{\text{rot}}(t)=\exp\left[-M^{1,k}_{2\,\text{rot}}\left(t\tau_\omega+\tau_\omega^2\left(e^{-t/\tau_\omega}-1\right)\right)\right]. \qquad (2)$$

τ_ω, the only variable parameter, is the angular momentum correlation time, roughly spoken the average time between two collisions of the molecule. There are two limiting cases of Eq. (2): in the "slow modulation" limit ($\tau_\omega \gg (M^{1,k}_{2\,\text{rot}})^{-1/2}$), Eq. (2) predicts Gaussian free rotor correlation functions whereas in the "fast modulation" limit

$$(\tau_\omega \ll (M^{1,k}_{2\,\text{rot}})^{-1/2})$$

simple exponential rotational diffusion correlation functions (Debye limit) are obtained. $M^{1,k}_{2\,\text{rot}}$ is the rotational second moment and given for a parallel infrared band (ν_{16} of C_6H_{12}) by [15]:

$$M^{1,0}_{2\,\text{rot}}=2kT/I_x \qquad (3)$$

but for a perpendicular band (ν_{29}, ν_{30} and ν_{31} of C_6H_{12}) by [15]:

$$M^{1,1}_{2\,\text{rot}}=kT/I_x+(1-\zeta)^2(kT/I_z)\,. \qquad (4)$$

I_x and I_z are the moments of inertia perpendicular and parallel to the symmetry axes ($C_6H_{12}: Ix = 193.7\ 10^{-40}$ g cm^2; $I_z = 343.5\ 10^{-40}$ g cm^2) [6], k is the Boltzmann constant and T is the temperature in K. The influence of the value of the Coriolis coupling constant ζ in rotational relaxation functions of the degenerate bands may be seen from Eq. (4): a large positive value of ζ (all other parameters at fixed values) leads to slower decaying correlation functions resp. smaller half widths and vice versa. The Coriolis coupling constants for the ir active fundamental vibrations of C_6H_{12} are given in [3] for the vapour phase:

$$\zeta_{29}=-0.373;\quad \zeta_{30}=+0.451;\quad \zeta_{31}=-0.469\,.$$

With respect to these values, at fixed temperature (and hence τ_ω), the fastest decaying reorientational correlation functions are obtained from ν_{31}, followed by ν_{29}, ν_{16} and ν_{30} (via Equation (2)). In fact, the experimental correlation times (Fig. 1) follow a similar pattern, although they also contain the contributions of vibrational relaxation. ν_{30} (with $\zeta_{30}=+0.451$) gives the largest experimental correlation times. ν_{16}, ν_{29} and ν_{31} give quite similar reorientational correlation times and in fact (for ν_{29} and ν_{31}) similar experimental correlation times. The values for ν_{16} are somewhat larger. So it might be concluded that vibrational relaxation gives only a minor contribution to the correlation functions. The situation changes, however, if values for the angular momentum correlation times are inserted into Eq. (2) and $C^{1,k}_{\text{rot}}(t)$ is calculated. Anisotropic Raman spectra of ν_4 of C_6H_{12} have been recently used to calculate τ_ω at 283 K (0.052 ps), 303 K (0.057 ps), 323 K (0.061 ps) and 343 K (0.067 ps)

[17]. Together with Eq. (3) resp. Eq. (4), the calculation of $C^{1,0}_{\text{rot}}(t)$ (for ν_{16}) resp. $C^{1,1}_{\text{rot}}(t)$ (for ν_{29}, ν_{30} and ν_{31}) can be carried out. If use is made of Eq. (1), the vibrational relaxation functions $\Phi_{\text{vib}}(t)$ may be extracted. The procedure is demonstrated in Fig. (2), where for ν_{29} the experimental relaxation function $\Phi_{\text{ir}}(t) = \text{FT}\, I(\tilde{\nu})_{\text{ir}}$ is compared with $C^{1,1}_{\text{rot}}(t)$ and $\Phi_{\text{vib}}(t)$ at different temperatures. For the remaining vibrations, similar results are obtained. The correlation times of the calculated reorientational correlation functions ($\tau_{1\,\text{rot}}$) and of the extracted vibrational relaxation functions (τ_{vib}) are included for all vibrations studied here in Figure 1. The following conclusions may be drawn from Figs. 1 and 2: reorientational relaxation, which occurs close to the Debye limit, gives only a small contribution to the over all correlation functions of ν_{16}, ν_{29}, ν_{30} and ν_{31}. Relaxation occurs mainly via vibrational relaxation, where the rate of relaxation $((\tau_{\text{vib}})^{-1})$ increases with increasing temperature and is (at given temperature) very different for the four vibrations studied.

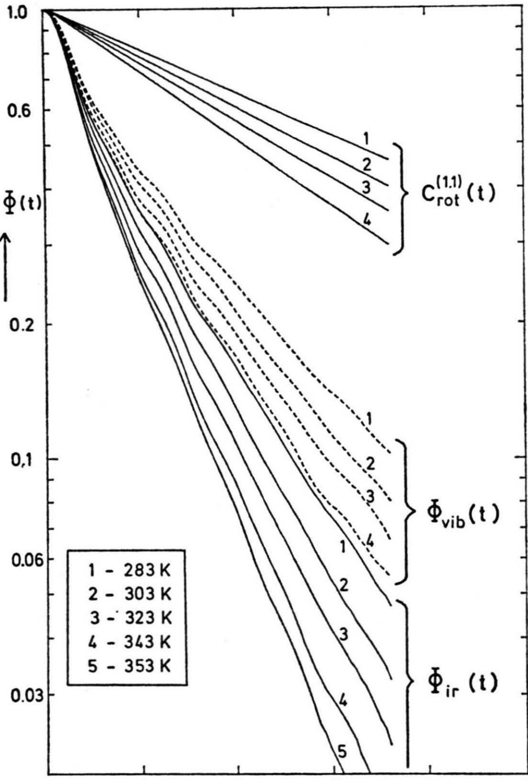

Fig. 2. Comparison of experimental, calculated reorientational and extracted vibrational correlation functions of ν_{29} of C_6H_{12} at different temperatures.

With regard to the models of vibrational relaxation these results are somewhat unsatisfactory. If long range interaction forces (e.g. dispersive forces) are responsible for vibrational relaxation via dephasing, "motional narrowing" of the intrinsic widths resp. slower decaying vibrational correlation functions are expected when the temperature is increased, opposite to the results found here [18—20]. Models of energy relaxation propose a similar temperature dependence of τ_{vib} [21]. If short range interactions (e.g. pure repulsive forces) are considered, the model of Fischer and Laubereau for pure dephasing [21] leads to relaxation rates which are in a first order of approximation proportional to T/τ_c (τ_c is the time between two collisions and may be approximated by τ_ω) and hence essentially independent of temperature [22]. Also it may seem to be difficult to expalin that the three similar degenerate vibrations ν_{29}, ν_{30} and ν_{31} (all CH_2 deformation modes [3] differ so much in their vibrational relaxation rates (see Figure 1).

However, the uncertainties introduced by the method used to extract the intrinsic line widths should be kept in mind. For example, rotation-vibration coupling may cause that Eq. (1) is not rigorously valid [23, 24]. Furthermore, the Coriolis constants given for the vapour phase have been used. Uncertainties could also be introduced by the angular momentum correlation times ($\pm 15\%$). Also the model used ("Kubo model", Eq. (2)) implies that the angular momentum correlation times of and around the main symmetry axis are identical. This point should be discussed in more detail.

In the rotational diffusion limit — and in liquid C_6H_{12} reorientation occurs close to this limit — two different diffusion constants $D^{\perp}$ and $D^{\parallel}$ are defined for the "tumbling" and the "spinning" motion. Hence there are two angular momentum correlation times $\tau^{\perp}_{\omega}$ and $\tau^{\parallel}_{\omega}$ related to $D^{\perp}$ and $D^{\parallel}$ via [7]:

$$\tau^{\perp}_{\omega} = \frac{D^{\perp} I_x}{k T}, \quad \tau^{\parallel}_{\omega} = \frac{D^{\parallel} I_z}{k T}. \tag{5}$$

If $\tau^{\perp}_{\omega}$ (or $D^{\perp}$) is known from a Raman experiment, $\tau^{\parallel}_{\omega}$ (or $D^{\parallel}$) may be extracted from ^{1}H-NMR T_1 data. This procedure is well established (although mainly for deuterated molecules) and carried out for C_6H_{12} in a recent paper of Tanabe [25]. At room temperature, a value of $\tau^{\perp}_{\omega} = 0.057$ ps is obtained from $D^{\perp}$

(which agrees well with our value at 303 K). But from the combination with the NMR reorientational correlation time τ_θ, a nearly three times larger value of $\tau_\omega^{\parallel}$ is computed from $D^{\parallel}$. That means a large anisotropy in angular momentum relaxation which might be explained by a "spinning" motion much less hindered than the "tumbling" motion. This seems to be quite unreasonable because it is well known from viscosity data that C_6H_{12} has a nearly spherical shape [26].

However, the uncertainties introduced by combining NMR and Raman results should be kept in mind. Tanabe uses a value of $\tau_\theta = 1.27$ ps from a study of O'Reilly et al. [27], but the ± 0.15 ps error of this value leads to a change in $\tau_\omega^{\parallel}$ by a factor of 3. Zeidler [28] gives a value of $\tau_\theta = 5.0$ ps which would lead to a $\tau_\omega^{\parallel}$ much smaller than $\tau_\omega^{\perp}$.

Support for assuming $\tau_\omega^{\perp} \approx \tau_\omega^{\parallel}$ comes from another ^{1}H-NMR-T_1 study of Pajak et al. on cyclohexene [29]. Because $I_x \approx I_y$, the asymmetric rotator C_6H_{10} behaves like a symmetric top molecule, and $D^{\perp}$ and $D^{\parallel}$ may be calculated from the NMR experiment alone. The moments of inertia and the shape of this molecule are very similar to C_6H_{12} ($I_x = 184 \cdot 10^{-40} \approx I_y = 178 \cdot 10^{-40}$ g cm^2; $I_z = 328 \cdot 10^{-40}$ g cm^2), and hence a similar reorientational behaviour may be expected. In the paper referred to, $D^{\perp}$ and $D^{\parallel}$ are determined at different temperatures for an infinite dilution in CCl_4. E.g., at 293 K values of $\tau_\omega^{\perp} = 0.044$ ps and $\tau_\omega^{\parallel} = 0.037$ ps; at 313 K values of $\tau_\omega^{\perp} = 0.049$ ps and $\tau_\omega^{\parallel} = 0.046$ ps are computed. These results propose a quite isotropic reorientation according to angular momentum relaxation for C_6H_{10} and should confirm our assumption that also in C_6H_{12} $\tau_\omega^{\perp}$ and $\tau_\omega^{\parallel}$ differ not too much to affect seriously our results.

On the other hand, there are other examples of increasing vibrational relaxation rates with increasing temperature [5] (even for C_6H_{12} [6, 12]) and it is well known that each mode of a molecule may contain a different contribution from the inner line width [30—32].

Obviously further investigations are needed to explain a vibrational relaxation in liquid cyclohexane. Especially a spectroscopic study in dilution with polar and non polar solvents might be helpful [31]. To explain the differences between ν_{29}, ν_{30} and ν_{31}, one must look very carefully to the actual normal coordinate displacements. Nevertheless, the results presented here may be regarded as a starting point for such studies which are now planned to be carried out.

Acknowledgements

Thanks are due to the Deutsche Forschungsgemeinschaft and the NATO.

[1] S. Bratos, J. Rios, and Y. Guissani, J. Chem. Phys. **52**, 439 (1970).

[2] D. R. Jones, H. C. Andersen, and R. Pecora, Chem. Phys. **9**, 339 (1975).

[3] K. B. Wiberg and A. Shrake, Spectrochim. Acta Part A **27**, 1139 (1971) and Part A **29**, 583 (1973).

[4] F. J. Bartoli and T. A. Litovitz, J. Chem. Phys. **56**, 404, 413 (1972).

[5] K. Tanabe and J. Jonas, J. Chem. Phys. **67**, 4222 (1977).

[6] R. Arndt and R. E. D. McClung, J. Chem. Phys. **70**, 5598 (1979).

[7] T. Bien, M. Possiel, G. Döge, J. Yarwood, and K. E. Arnold, Chem. Phys. **56**, 203 (1981).

[8] J. Schulz, Z. Naturforsch. Teil A **29**, 1636 (1974).

[9] M. L. Bansal and P. A. Roy, Chem. Phys. Letters **50**, 513 (1977).

[10] M. L. Bansal and P. A. Roy, Mol. Phys. **38**, 1419 (1979).

[11] W. Reimschüssel and H. Abramczyk, Chem. Phys. Letters **73**, 565 (1980).

[12] K. Tanabe and J. Jonas, Chem. Phys. **38**, 131 (1979).

[13] K. Tanabe and J. Hiraishi, Mol. Phys. **39**, 1507 (1980).

[14] R. G. Gordon, J. Chem. Phys. **44**, 1830 (1966).

[15] M. Gilbert, P. Nectoux, and M. Drifford, J. Chem. Phys. **68**, 679 (1978).

[16] R. Kubo, in: Fluctuation, Relaxation and Resonance in Magnetic Systems, edited by D. ter Haar (Oliver and Boyd, Edinburgh 1962), pp. 23 ff.

[17] a) T. Bien and G. Döge, J. Raman Spectrosc. in press. b) T. Bien, P. H. D. Thesis, Braunschweig 1981.

[18] G. Döge, Z. Naturforsch. Teil A **28**, 919 (1973).

[19] P. C. M. van Woerkom, J. de Bleyser, M. de Zwart, and J. C. Leyte, Chem. Phys. **4**, 236 (1974).

[20] W. G. Rothschild, J. Chem. Phys. **65**, 455 (1976).

[21] J. F. Fischer and A. Laubereau, Chem. Phys. Letters **35**, 6 (1976).

[22] J. Schroeder, V. H. Schiemann, P. T. Sharko, and J. Jonas, J. Chem. Phys. **66**, 3215 (1977).

[23] A. M. Amorim Da Costa, M. A. Norman, and J. H. R. Clarke, Mol. Phys. **29**, 191 (1975).

[24] S. Miller and J. H. R. Clarke, Chem. Phys. Letters **56**, 235 (1978).

[25] K. Tanabe, Chem. Phys. Letters **83**, 397 (1981).

[26] L. H. Thomas, Trans. Faraday Soc. **62**, 328 (1966).

[27] D. E. O'Reilly, E. M. Peterson, and D. L. Hogenboom, J. Chem. Phys. **57**, 3969 (1972).

[28] M. D. Zeidler, Ber. Bunsen Ges. **69**, 659 (1965).

[29] Z. Pajak, L. Latanowics, and K. Jurga, Ber. Bunsen Ges. **84**, 769 (1980).

[30] R. Arndt, G. Döge, and A. Khuen, Chem. Phys. **21**, 53 (1977).

[31] R. Arndt, G. Döge, and J. Yarwood, Chem. Phys. **25**, 387 (1977).

[32] W. G. Rothschild, G. J. Rosasco, and R. C. Livingston, J. Chem. Phys. **62**, 1253 (1975).