Temperature Dependence of Reorientational and Vibrational Relaxation Times of Benzene and Benzene-d_6 in Solid and Liquid Phases

Hiroyasu NOMURA,* Shinobu KODA,** and Yutaka MIYAHARA

Department of Chemical Engineering, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

***Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464*

(Received December 26, 1978)

The temperature dependences of reorientational and vibrational relaxation times of benzene and benzene-d_6 in the solid and liquid phases were measured by means of Raman line shape analysis. The temperature dependence of the reorientational relaxation times was in very good agreement with that published previously. The vibrational relaxation times of benzene changed drastically at the solid to liquid phase transition point both in C_6H_6 and C_6D_6. We consider that this effect is due to the non-radiative energy transfer and the pure dephasing process by molecular collisions in the liquid state.

Some time ago, the ultrasonic technique was the only method available to measure the vibrational relaxation times of molecules in the liquid state.[1] However, more recently some other methods have been used to study the molecular orientational and vibrational relaxation processes in the liquid phase. In particular, it is known that one may analyse separately the effects of reorientational and vibrational motions from the profiles of the isotropic and anisotropic Raman scattering. Also, spectroscopic techniques using high powered pulsed laser have been applied to the investigation of vibrational relaxation in liquids.[2-5]

Recently, Griffiths, Clerc, and Rentzepis applied the Raman and picosecond pulsed spectroscopic methods to study the intermolecular vibrational energy transfer between C_6H_6 and C_6D_6.[6]

Several mechanisms may contribute to the shape of the vibrational correlation function, but the two most common interpretations are energy relaxation to lower vibrational levels (the lowest of which is the ground vibrational state) through a collisional non-radiative mechanism, and phase relaxation, which also involves a collision induced process. Both mechanisms are subject to molecular collisions in the liquid phase.

An intuitive argument suggests that the molecules in the solid phase freeze out orientational motions and collisions, which are effective for the exchange of the energy. Therefore the vibrational relaxation time in the solid state is expected to be much longer than in the liquid state. A discontinuity in the vibrational relaxation times is expected at the solid-liquid phase change.

In this work, we report the experimental results of the temperature dependence of the reorientational and vibrational relaxation times of C_6H_6 and C_6D_6 in solid and liquid phases and discuss the process of the vibrational energy transfer of C_6H_6 and C_6D_6 in the liquid phase.

Experimental Details and Data Analysis

The apparatus used consisted of an argon ion laser (800 mW at 488 nm) produced by the Coherent Radiation Co., Ltd., and a Laser Raman Spectrometer of JRS-Ul type JEOL, Ltd., Japan.

In order to obtain the reorientational and vibrational relaxation times, the Raman line shapes of the $\nu_2(a_{1g})$ and $\nu_1(a_{1g})$ fundamental modes of ring and C–H or C–D stretching were analyzed. The Raman spectrum was observed at 90° with respect to the linearly polarized incident light. With $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ respecting the strong and weak components of the scattered light, one can write:

$$I_{\parallel}(\omega) = I_{\mathrm{isot}}(\omega) + 4/3\, I_{\mathrm{anis}}(\omega) \quad (1)$$

$$I_{\perp}(\omega) = I_{\mathrm{anis}}(\omega) \quad (2)$$

$$\rho_s = I_{\perp}(\omega)/I_{\parallel}(\omega) \quad (3)$$

where ρ_s is the depolarization ratio. $I_{\mathrm{isot}}(\omega)$ represents the intrinsic vibrational line shape, and $I_{\mathrm{anis}}(\omega)$ is a convolution of the vibrational line shape and the orientational spectrum.

The Raman lines of C_6H_6 and C_6D_6 were measured using a constant mechanical slit width, 30 μm. The Raman bands obtained are broadened by the slit and the spectrum measured is a convolution of the true Lorentzian spectrum and the slit function, $S(\omega)$. As the spectral slit function is well approximated by a Gaussian function,[7] one can write

$$I(\nu) = N\int_{-\infty}^{\infty} \frac{1}{\beta_L^2+(\nu-\nu')^2}\exp\left\{-\left(\frac{\nu'}{\beta_g}\right)^2\right\}d\nu' \quad (4)$$

where β_L is the true half-width and $\beta_g = S/2\sqrt{\ln 2}$,[8] where S is the spectral slit width; $S=0.741$ cm^{-1} at 30 μm. By curve fitting of Eq. 4 to the measured spectrum, we determined the true half-width β_L of each measured Raman line. $\omega_{\mathrm{isot}}(1/2)$ and $\omega_{\mathrm{anis}}(1/2)$, hereafter, refer to the true half-width, β_L, of the isotropic and anisotropic Raman line, respectively. From $I_{\parallel}(\omega)$ of the $\nu_2(a_{1g})$ band of C_6D_6 in the liquid phase, the $\omega_{\mathrm{isot}}(1/2)$ obtained was 0.73 cm^{-1}, corresponding to a vibrational relaxation time of 7.42×10^{-12} s. This value is in excellent agreement with that obtained by Griffiths *et al.* from direct measurements using picosecond spectroscopy and the Raman line width.

Temperatures were in the range from −50 to 60 °C. A variable temperature Raman cell of the Harney-Miller type was used.

Results

The temperature dependence of $\omega_{\mathrm{isot}}(1/2)$ and $\omega_{\mathrm{anis}}(1/2)$ of ν_1 and ν_2 bands of C_6H_6 are shown in Fig. 1 and those of ν_1 and ν_2 bands of C_6D_6 are shown in Fig. 2, together with the values obtained by Griffiths *et al.*[9] In Figs. 1 and 2, in the solid phase, $\omega_{\mathrm{anis}}(1/2)$ apparently equals $\omega_{\mathrm{isot}}(1/2)$ for C_6H_6 and C_6D_6 at each Raman line but, as pointed out by many workers,[10,11] we can not directly reduce the above relation in the crystalline state from this experimental

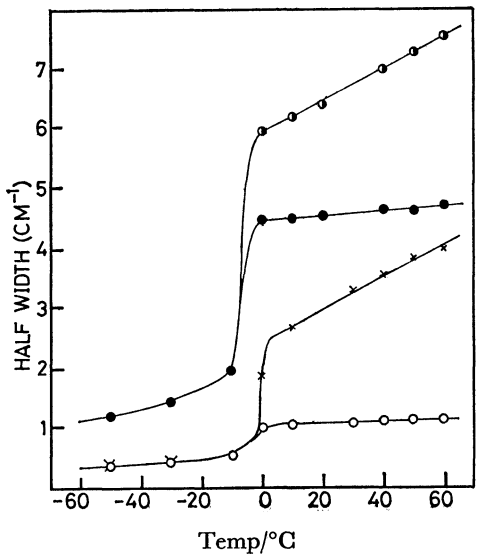

Fig. 1. Temperature dependences of half-width of ν_1 and ν_2 bands of C_6H_6. ●; $\omega_{isot}(1/2)$ of ν_1 band, ◑; $\omega_{anis}(1/2)$ of ν_1 band, ○; $\omega_{isot}(1/2)$ of ν_2 band, ×; $\omega_{anis}(1/2)$ of ν_2 band.

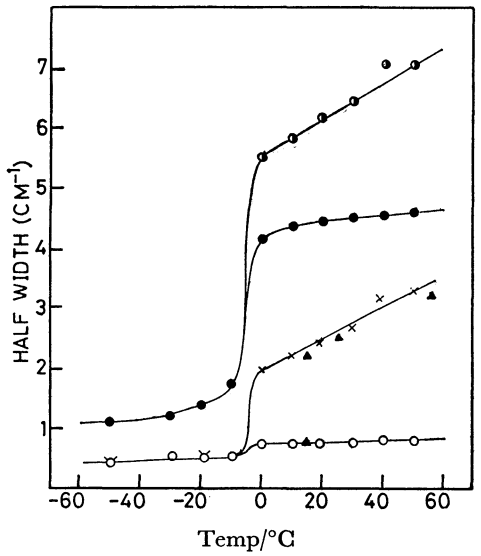

Fig. 2. Temperature dependences of half-width of ν_1 and ν_2 bands of C_6D_6. ▲; $\omega_{anis}(1/2)$ of ν_2 band (Griffiths *et al.*) and the other symbols are the same as those in Fig. 1.

data. However, as the Raman intensities of the isotropic light were very much stronger than those of the anisotropic light, the values of $\omega_{isot}(1/2)$ in the solid state may be considered significant.

As is seen in Figs. 1 and 2, the values of $\omega_{isot}(1/2)$ are dependent on the vibrational modes and increase slightly with increasing temperature in the solid and liquid phases.

From these results, we can obtain the vibrational and reorientational relaxation times from the following equations:

$$\tau_v = (2\pi c\omega_{isot}(1/2))^{-1} \quad (5)$$

$$\tau_{or} = (2\pi c\omega_{or}(1/2))^{-1} \quad (6)$$

where $\omega_{or}(1/2)=\omega_{anis}(1/2)-\omega_{isot}(1/2)$.

Discussion

Reorientational Relaxation Times of C_6H_6 and C_6D_6. The relationship between ln τ_{or} and $10^3/T$ is shown in Fig. 3. As is seen in Fig. 3, the reorientational relaxation times of C_6H_6 and C_6D_6 obtained from the ν_2 bands are in good agreement with those obtained from their ν_1 bands. The isotope effect, $\tau_{or}(C_6D_6)/\tau_{or}(C_6H_6)=1.102$, is in good agreement with the value calculated for the small step Brownian diffusion (1.10).

The relationship between ln τ_{or} and T can be expressed by

$$\ln \tau_{or} = A + \Delta U/RT \quad (7)$$

The values of ΔU are 2.83 and 2.76$_4$ kcal/mol for C_6H_6 and C_6D_6, respectively. These values are in very good agreement with those published previously.[9]

Vibrational Relaxation Times of ν_1 and ν_2 Modes. As is seen in Figs. 1 and 2, the half-widths of ν_2 fundamentals in C_6H_6 and C_6D_6 are 1.09 and 0.72 cm^{-1} at 30 °C and slightly depend on the temperature.

Griffiths *et al.* explained this difference as follows.[6] During collisions, the vibrational energy from one molecule is more readily transferred to a lower neighboring energy level in a second molecule if the vibrational energy levels are close together. In C_6H_6, there are two vibrational levels, ν_7 at 985 (b_{2g}) and ν_{19} at 970 (e_{2u}) cm^{-1}. During collisions, the near resonance energy condition would favor the non-radiative transition. On the contrary, the closest level in C_6D_6 is the $\nu_{17}(e_{2g})$ fundamental at 867 cm^{-1}. The energy difference between the $\nu_2(a_{1g})$ and the $\nu_{17}(e_{2g})$ fundamental modes is $\Delta E=78$ cm^{-1} in C_6D_6. This value is much larger than the energy differences $\Delta E=6$ cm^{-1} between the $\nu_2(a_{1g})$ and the $\nu_7(b_{2g})$, and $\Delta E=21$ cm^{-1} between the $\nu_2(a_{1g})$ and the $\nu_{19}(e_{2u})$. Therefore, in C_6D_6 a non-radiative transition such as is observed in C_6H_6 should not contribute significantly to a change in life time of the ν_2 state of C_6D_6. Although there is one more level, $\nu_6(b_{1u})$, at 963 cm^{-1} near the ν_2 fundamental, this excitation energy level is higher

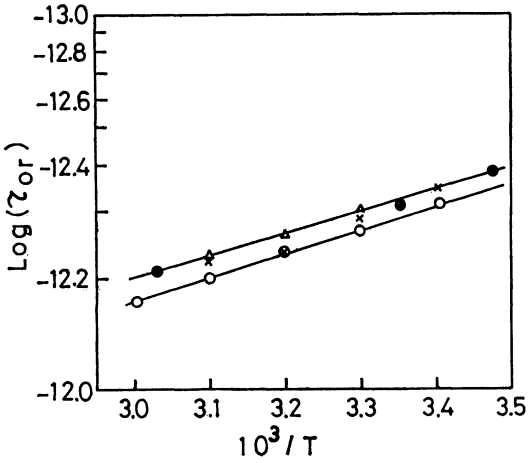

Fig. 3. Relationships between log (τ_{or}) and $10^3/T$. ○; C_6H_6, obtained from ν_2 band, ●; C_6D_6, obtained from ν_2 band, △; C_6D_6, Griffiths *et al.*, ×; C_6D_6, obtained from ν_1 band.

than ν_2 at 945 cm^{-1}; so this level may not contribute significantly to the relaxation mechanism of the ν_2 mode of C_6D_6.

At the transition point, the values of $\omega_{isot}(1/2)$ for C_6D_6 changed from 0.52 in solid state to 0.72 cm^{-1} in liquid state. This broadening can only be interpreted by considering some other mechanisms besides those proposed by Griffiths *et al.*

Similarly, as is seen in Figs. 1 and 2, the half-widths of the ν_1 fundamental mode are broader than those of the ν_2 mode in liquid phase. The differences in $\omega_{isot}(1/2)$ of ν_1 solid and liquid phases are about 2.8 cm^{-1}, which is about 6 and 10 times those of the ν_2 band of C_6H_6 and C_6D_6, respectively.

As mentioned above, there is one more dominant mechanism which contributes to the vibrational relaxation, that is, the phase relaxation or so-called "pure dephasing process,"

Fischer and Laubereau[12] have presented the following expression for the vibrational dephasing relaxation time:

$$\tau_{ph} = \frac{2}{9}\frac{M^2\omega^2L^2}{\mu\gamma^4k_BT}\tau_c \qquad (8)$$

where M is the reduced mass of the oscillator with frequency ω, and L measures the range of interactions between colliding molecules. The μ and γ are parameters defined by them.[12]

As a first approximation, the energy dissipation and pure dephasing which are caused by the molecular collisions in liquid phase are considered to be an independent process. The vibrational relaxation time of this mechanism, τ_v', can be written as follows:

$$1/\tau_v' = 1/\tau_{ph} + 1/\tau_e \qquad (9)$$

in a practical case, $(1/\tau_v')$ can be estimated from the difference of $\omega_{isot}(1/2)$ between the solid and the liquid phase. In ultrasonic studies of liquid C_6H_6 and C_6D_6, the relaxation process was found to have the frequency of about 2 GHz.[13,14] This relaxation has been considered to be due to the vibrational process. The total relaxation strength of the ultrasonic relaxation was found to be in very good agreement with those calculated from the Einstein equation, assuming the relaxation to be that of vibrational specific heats. From these ultrasonic data and a liquid model, τ_e in Eq. 8 can be estimated as about 0.79×10^{-13} s.[1]

Recently, Tanabe and Jonas have reported that the line broadening effects of Raman lines can be interpreted by the pure dephasing model as caused by the molecular collisions in the liquid phase, using Eq. 8.[15,16] The values obtained are summarized in Table 1. The vibrational relaxation mechanism of ν_2 band in the liquid C_6H_6 involves the non-radiative transition mentioned above. So, as is seen in Table 1, the difference of the $\omega_{isot}(1/2)$ of ν_2 band between in C_6H_6 and C_6D_6, about 0.3 cm^{-1}, can be considered to be due to the non-radiative transition mechanism proposed by Griffiths *et al.* In the case of ν_1 band, the value of δ_v' of C_6H_6 is comparable to that of C_6D_6.

As indicated in Table 1, the values of δ_v' obtained in this experiment are quite different from those of δ_{ph} estimated from Eq. 8. In the dephasing mechanism explained by Eq. 8, a binary collision is assumed and only the repulsive part of the intermolecular potential is considered. Intrinsically, the above dephasing mechanism should be applied to the diatomic molecule. In a polyatomic molecule such as benzene, the interactions between intramolecular modes should be involved. Recently, the vibrational dephasing of polyatomic molecules was treated by the intermolecular vibrational energy exchange model.[17] In the exchange model, the dephasing arises from random modulation of the vibrational frequency caused by intramolecular anharmonic coupling to low frequency modes which are undergoing intermolecular energy exchange with the bath. Therefore, the δ_v' obtained in this experiment could not be explained by the dephasing mechanism expressed by Eq. 8.

Table 1. Estimated vibrational widths (cm^{-1})

Mode	Assignment	C_6H_6		C_6D_6	
		δ_v'	δ_{ph}	δ_v'	δ_{ph}
$\nu_1(a_{1g})$	C-H or C-D stretching	2.8	6.3_5[a]	2.8	3.5_5[a]
$\nu_2(a_{1g})$	C-C stretching	0.5	0.4_0[a]	0.2	0.4_5[a]

a) The dephasing widths calculated by Tanabe and Jonas.[15]

$\delta_v' = (2\pi c\tau_v')^{-1}$ and $\delta_{ph} = (2\pi c\tau_{ph})^{-1}$.

In the C–H or C–D stretching vibration region, there are a few Raman forbidden bands; for example, the 2264 and 2294 cm^{-1} bands which lie close to ν_1 band of C_6D_6. At this stage, it is impossible to rule out the energy transfer mechanism due to the non-radiative transition as in the case of ν_2 band of C_6H_6.

As indicated above, the vibrational relaxation mechanism of benzene is very complicated. Further theoretical and experimental investigations are needed and continuing.

The authors are grateful to Prof. D. Nakamura of Nagoya University for many stimulating discussions. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York (1950).
2) A. Laubereau, D. von der Linde, and W. Kaiser, *Phys. Rev. Lett.*, **28**, 1162 (1972).
3) R. R. Alfano and S. L. Shapiro, *Phys. Rev. Lett.*, **29**, 1655 (1972).
4) A. Laubereau, L. Kirshner, and W. Kaiser, *Opt. Commun.*, **9**, 128 (1973).
5) P. R. Monson, S. Patumtevatibal, K. J. Kaufmann, and G. W. Robinson, *Chem. Phys. Lett.*, **28**, 312 (1974).
6) J. E. Griffiths, M. Clerc, and P. M. Rentzepis, *J. Chem. Phys.*, **60**, 3824 (1974).
7) R. E. Meredith. *J. Quant. Spectros. Radiant. Transfer*, **12**, 455 (1972).
8) J. S. Seshadri and R. Norman Jones, *Spectrochim. Acta*, **19**, 1013 (1963).
9) K. T. Gillen and J. E. Griffiths, *Chem. Phys. Lett.*, **17**, 359 (1972).

10) B. J. Bulkin, *J. Opt. Soc. Am.*, **59**, 1387 (1969).
11) D. W. Johnson and D. Sutton, *Can. J. Chem.*, **49**, 671 (1971).
12) S. F. Fischer and A. Laubereau, *Chem. Phys. Lett.*, **35**, 6, (1975).
13) K. Takagi, P-K Choi, and K. Negishi, *Acoustica*, **34**, 336 (1976).
14) K. G. Plass, *Acoustica*, **19**, 236, (1967/68).
15) K. Tanabe and J. Jonas, *J. Chem. Phys.*, **67**, 4222 (1977).
16) K. Tanabe and J. Jonas, *Chem. Phys. Lett.*, **53**, 278 (1978).
17) R. M. Shelby, C. B. Harris, and P. A. Cornelius, *J. Chem. Phys.*, **70**, 34 (1979).