Temperature Effects on the Raman Intensity of Liquid Samples and an Averaged Molecular Field

Haruo HATAKEYAMA and Tsunetake FUJIYAMA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received July 23, 1977)

The relative Raman intensities of the ν_1 line of carbon tetrachloride, the ν_8 line of acetonitrile, and the ν_3 line of chloroform were observed in the liquid phase and at various temperatures. The apparent intensity change due to the temperature were explained in terms of the local field effect, the density change, the statistical distribution effect, and the contribution of transition hyperpolarizability in the presence of a non-zero averaged molecular field.

Raman intensity measurements have a great advantage, in principle, over the intensity measurements of absorption spectra. They are free from the effects of a slit-function,[1] the effects related to anomalous dispersion,[2-6] the effects of multi-reflections inside sample layers,[7-10] the so-called baseline effects,[1,11] and so on, all of which are notorious difficulties in the intensity measurements of liquid samples by infrared absorption methods. Therefore, careful measurements of Raman intensities will afford useful information about intermolecular interactions in the liquid phase.

In our preceding report, the intermolecular interaction of a dipole-dipole type has been shown to be most important in explaining the concentration dependence of the Raman intensities in various binary solutions.[12] If the component molecules in solutions have dipole moments, there exists a non-zero averaged molecular field at a given molecule, and the contribution of the transition hyperpolarizability cannot be neglected in comparison with that of the transition polarizability. As the concentration dependence of the averaged molecular field results from the change in an intermolecular distance due to different concentrations,[13] the averaged molecular field and, therefore, the Raman intensity may be expected to be dependent on the temperature, also.

In the present report, the temperature effects on the Raman intensities were measured for three different liquid systems in order to study the role of the averaged molecular field which was produced by the dipole-dipole interaction. Carbon tetrachloride, acetonitrile, and chloroform were chosen because they were typical examples of a non-polar molecule, a molecule with a large dipole moment, and a molecule with a rather small dipole moment respectively.

Experimental

The spectrometer used for the present work was designed and constructed in our laboratory. The instrument was composed of a He-Ne gas laser source (NEC GLG 105, 15 mW), a grating monochromator (JEOL JSG 125B), a photomultiplier (HTV R374, S-20 response), a lock-in amplifier (NF LI-573), and a recorder.

The temperature of a sample cell ($10\times20\times40$ mm^3) was regulated by means of a thermostating box whose temperature was controlled by changing the electrical current supplied to nichrome heaters. The temperatures of the thermostating box and the sample cell were observed by means of a mercury thermometer and a thermocouple respectively. The temperature drift of the sample was less than ±1 K within the temperature range of 300—370 K.

The stability of the laser out-put during the individual spectral measurements was observed by monitoring the light energy which penetrated through the 100% reflectance mirror of the laser cavity. When the power of the laser source drifted more than 1% during the measurements, the data observed were completely discarded.

All the chemicals used in the present study were commercial products. The carbon tetrachloride and acetonitrile were purified by fractional distillations repeated three times. The chloroform was purified by column chromatography on alumina.

The Raman spectra were observed for the ν_1 line of carbon tetrachloride, the ν_8 line of acetonitrile, and the ν_3 line of chloroform. The Raman intensity was determined from the observed band area by means of the weight method. The observations were repeated four times for each temperature; their averaged values were then taken as the observed intensities. The deviations of the observed band areas from the averaged values were less than 2%.

Results and Discussion

ν_1 Line of Carbon Tetrachloride. The Raman intensities of the ν_1 line of liquid carbon tetrachloride were observed in the temperature range from 291 to 333 K. The observed relative intensity ratios are summarized in Table 1, where the relative intensity at 291 K serves as the standard. The relative intensity decreases about 8% as the temperature changes from 291 to 333 K.

Table 1. ν_1 Line of carbon tetrachloride

T/K	d/d_{291}	s/s_{291}	L/L_{291}	Lsd/Lsd_{291}	I/I_{291}
291	1.000	1.000	1.000	1.000	1.000
315	0.972	1.021	0.961	0.954	0.948
326	0.957	1.033	0.943	0.932	0.929
330	0.952	1.038	0.936	0.925	0.917

The apparent intensity change due to the temperature has been discussed in detail in a previous report,[14] where the effects of the density, the local field, and the statistical distribution of molecules in relation to a vibrational state have been emphasized. These factors are all temperature-dependent and should be taken into account in interpreting the present results.

The density, d, as a function of the temperature may be found in the International Critical Tables.[15] The relative values of the density at various temperatures,

d/d_{291}, are summarized in Table 1, where the density at 291 K is chosen as the standard.

The statistical factors, s, may be expressed as

$$s = \frac{1}{1-\exp(-hc\nu/kT)}, \quad (1)$$

where ν is the frequency displacement of a Raman line from that of the radiating wave; T, the absolute temperature; h, the Planck constant; k, the Boltzmann constant, and c, the velocity of light. The calculated relative values, s/s_{291}, are summarized in Table 1, where the s value at 291 K is taken as the standard.

The local-field correction in the Raman scattering, L, of the Eckhardt type may be expressed as[16]

$$L = \left(\frac{n^2+2}{3}\right)^4, \quad (2)$$

where n is the refractive index at the Stokes frequency. The calculated relative values of the local-field correction factors, L/L_{291}, are summarized in Table 1, where L at 291 K is taken as the standard. In the calculation, the refractive indices for the different temperatures were estimated from the density values found in the International Critical Tables and the empirical Eykman equation:

$$\frac{n^2-1}{n+0.4} = \frac{d}{M} \times C, \quad (3)$$

where C is a constant characteristic for a molecule, M, the molecular weight, and d, the density.[17]

Finally, the products of L, s, and d were calculated. They are summarized in Table 1 (designated as (Lsd)). The relative values, $(Lsd)/(Lsd)_{291}$, are expected to agree with those of the relative intensity, I/I_{291}, if the factors considered here contribute mainly to the apparent intensity change resulting from the change in the temperature. Actually, the agreement between these two sets of values is excellent.

Table 2. ν_8 Line of acetonitrile

T/K	d/d_{290}	s/s_{290}	L/L_{290}	Lsd/Lsd_{290}	I/I_{290}
290	1.000	1.000	1.000	1.000	1.000
301	0.981	1.016	0.980	0.977	0.950
305	0.974	1.022	0.974	0.969	0.929
314	0.963	1.031	0.962	0.955	0.900

ν_8 Line of Acetonitrile. The same procedure was applied to the ν_8 line of liquid acetonitrile in the temperature range from 290 to 314 K. The results are summarized in Table 2. It may be seen from the table that the apparent intensity ratio, I/I_{290}, of this line decreases about 10% as the temperature changes from 290 to 314 K, where the relative intensity at 290 K is chosen as the standard. On the other hand, the calculated correction factor, $(Lsd)/(Lsd)_{290}$, decreases only 5% within the same temperature range. The disagreement between these two sets of values is in good contrast with the excellent agreement found for the ν_1 line of carbon tetrachloride and can be ascribed mostly to the physical property of acetonitrile. Therefore, we will focus our attention on the role of the large dipole moment of acetonitrile in a consideration of the temperature dependence of the apparent intensities.

It has been shown in our previous report[12] that the apparent Raman intensity can be affected by the transition hyperpolarizability in the presence of an averaged molecular field produced by the dipole moments of the surrounding molecules. According to the theory, the Raman scattering cross section corresponding to the ν_8 line of acetonitrile, $\Omega(CH_3CN; \nu_8)$, is expressed as

$$\Omega(CH_3CN; \nu_8) \propto \frac{14}{15}(B + A\langle F_{0z}\rangle_{av}), \quad (4)$$

where

$$A = 2\{{}^{Q_8}(\alpha_1^\circ)_{xy}\,{}^{Q_8}(\beta_1^\circ)_{xyz} + {}^{Q_8}(\alpha_1^\circ)_{yz}\,{}^{Q_8}(\beta_1^\circ)_{yzz}\},$$
$$B = {}^{Q_8}(\alpha_1^\circ)_{xy}^2 + {}^{Q_8}(\alpha_1^\circ)_{yz}^2.$$

In the above equations, ${}^{Q_8}(\alpha_i^\circ)_{ij}$ and ${}^{Q_8}(\beta_i^\circ)_{ijk}$ are the i,j-element of the transition polarizability and the i,j,k-element of the transition hyperpolarizability tensor related with the normal coordinate, Q_8, respectively, and the i, j, and k refer to the molecular fixed Cartesian coordinates, with the molecular axis being chosen as the z-axis. In the case of the ν_8 line of acetonitrile, the A and B of Eq. 4 have been determined experimentally as

$$A = 15.308 \times 10^{-10}\ (\text{Å}^6\,\text{dyn}^{-1}\,\text{esu}),$$
$$B = 1.66 \times 10^{-3}\ (\text{Å}^6),$$

from the observation of the concentration dependence of the Raman intensity. $\langle F_{0z}\rangle_{av}$ is the averaged electric field produced at the position of a molecule by the influence of the surrounding molecules.

There are various types of intermolecular interactions which produce electric fields at the position of a given molecule in a liquid. The simplest and most important of these is the interaction of a dipole-dipole type. A molecule with a dipole moment affects the orientational distribution of surrounding molecules through dipole-dipole interactions. This results in the appearance of a non-zero averaged electric field at the position of the central dipole. For a pure liquid, this averaged electric field has been calculated to be[13]

$$\langle F_{0z}\rangle_{av} = \frac{4\pi^2}{27} N_a^2 \frac{\mu_0^3}{kT} \frac{\rho^2}{W_m^2} + \frac{2\pi^2}{25\times 243} N_a^2 \frac{\mu_0^7}{(kT)^3} \frac{\rho^4}{W_m^4}, \quad (5)$$

where μ_0 is a permanent dipole moment; ρ, the density; W_m, the molecular weight; k, the Boltzmann constant; T, the absolute temperature, and N_a the Avogadro number. Using the permanent dipole moment value of 3.92 D observed for acetonitrile,[18] the $\langle F_{0z}\rangle_{av}$ value is calculated to be of the order of 10^5 dyn esu^{-1}; the detailed results are shown in Table 3. Obviously, the $\langle F_{0z}\rangle_{av}$ value is temperature-dependent. By inserting the numerical values of A, B, and $\langle F_{0z}\rangle_{av}$ into Eq. 4, the relative magnitudes of the scattering cross sections were calculated for the various temperatures. Obviously, the calculated relative scattering cross sections, Ω/Ω_{290}, are temperature-dependent. The products of the calculated relative scattering cross sections, Ω/Ω_{290}, and the relative correction factors, Lsd/Lsd_{290}, are in good agreement with the observed

Table 3. Averaged molecular field and Raman intensity for ν_8 line of acetonitrile

T/K	$\langle F_{0z}\rangle_{av}$ (dyn esu^{-1})	Ω/Ω_{290}	$\frac{\Omega \cdot Lsd}{\Omega_{290} \cdot Lsd_{290}}$	I/I_{290}
290	4.31×10^5	1.000	1.000	1.000
301	3.81×10^5	0.967	0.944	0.950
305	3.66×10^5	0.957	0.927	0.929
314	3.40×10^5	0.940	0.900	0.900

relative intensities, I/I_{290}. This result shows that the transition hyperpolarizability derivative plays an important role in producing the apparent temperature dependence of the Raman intensity under the existence of a considerable magnitude of $\langle F_{0z}\rangle_{av}$.

ν_3 Line of Chloroform. Exactly the same procedures were applied to the ν_3 line of liquid chloroform. The results are summarized in Table 4. It can be seen from the table that the relative intensity of this line decreases about 8% as the temperature changes from 292 to 320 K, while the calculated correction factor, $(Lsd)/(Lsd)_{292}$, decreases about 3%. It is clear that the discrepancy between the observed and the calculated intensity ratios can hardly be explained by the effect of the averaged molecular field, $\langle F_{0z}\rangle_{av}$.

Table 4. ν_3 Line of choroform

T/K	d/d_{292}	s/s_{292}	L/L_{292}	Lsd/Lsd_{292}	I/I_{292}
292	1.000	1.000	1.000	1.000	1.000
305	0.983	1.013	0.977	0.973	0.974
312	0.975	1.022	0.966	0.963	0.950
320	0.964	1.032	0.954	0.950	0.923

The scattering cross section of this line, including the effect of the averaged molecular field, can be expressed as[12]

$$\Omega(CHCl_3;\ \nu_3) \propto \frac{1}{15}(B + A\langle F_{0z}\rangle_{av}),$$

where

$$\begin{aligned} A &= 18^{Q_3}(\alpha_1^\circ)_{xx}{}^{Q_3}(\beta_1^\circ)_{xxz} + 8^{Q_3}(\alpha_1^\circ)_{zz}{}^{Q_3}(\beta_1^\circ)_{zzz} \\ &\quad + 2^{Q_3}(\alpha_1^\circ)_{xx}{}^{Q_3}(\beta_1^\circ)_{zzz} + 2^{Q_3}(\alpha_1^\circ)_{zz}{}^{Q_3}(\beta_1^\circ)_{xxz}, \qquad (6) \\ B &= 9^{Q_3}(\alpha_1^\circ)_{xx}^2 + 2^{Q_3}(\alpha_1^\circ)_{xx}{}^{Q_3}(\alpha_1^\circ)_{zz} + 4^{Q_3}(\alpha_1^\circ)_{zz}^2. \end{aligned}$$

The magnitude of $\langle F_{0z}\rangle_{av}$ can be calculated from Eq. 5 using the dipole moment value of 1.05 D for chloroform.[19] The $\langle F_{0z}\rangle_{av}$ value of chloroform is of the order of 10^3 dyn esu^{-1}, which is about hundredth of that for acetonitrile. As the magnitude of A for chloroform may be expected to be as large as that for acetonitrile, the effect of $\langle F_{0z}\rangle_{av}$ on the Raman intensity is negligibly small. Therefore, the discrepancy between the observed and the calculated intensity ratios corresponds to the real change in the transition polarizability of this line on passing from 292 to 320 K; this can be explained with respect to the direct intermolecular interactions, such as the break-down of hydrogen bonding between chloroform molecules in the liquid phase on the elevating of the temperature. It is important to add that the relative intensity changes its magnitude about 20% as the temperature changes from 297 to 313 K in the case of the ν_2 line of liquid chloroform, while the correction factor, $(Lsd)/(Lsd)_{297}$ decreases only 6%.[14] This discrepancy may originate from the same type of intermolecular interaction.

Averaged Molecular Field and Conclusions. A few important conclusions can be drawn from the present results. In most cases, the effects of the L, s, and d factors make the observed Raman intensities temperature-dependent. When a component molecule has a large dipole moment, the Raman intensity is temperature-dependent because of the existence of a non-zero averaged molecular field, $\langle F_{0z}\rangle_{av}$, in the liquid phase. If the magnitude of $\langle F_{0z}\rangle_{av}$ is of the order of 10^5 dyn esu^{-1} or more, the Raman intensity is determined not only by the transition polarizabilities (the first term of Eq. 4 or 6) but also by the transition hyperpolarizabilities (the second term of Eq. 4 or 6).

References

1) K. S. Sehardi and R. N. Jones, *Spectrochim. Acta*, **19**, 1013 (1963).
2) P. N. Schatz, *Spectrochim. Acta*, **21**, 617 (1965).
3) S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).
4) H. E. Hallman, "Infrared Spectra and Molecular Structure," Chapt. XII, Elsevier, N.Y. (1963).
5) A. A. Clifford and B. L. Crawford, Jr., *J. Phys. Chem.*, **70**, 1536 (1966).
6) T. Fujiyama and B. L. Crawford, Jr., *J. Phys. Chem.*, **72**, 2174 (1968).
7) M. Yasumi, *Bull. Chem. Soc. Jpn.*, **28**, 489 (1955).
8) S. Maeda and P. N. Schatz, *J. Chem. Phys.*, **35**, 1617 (1961).
9) J. V. White and W. M. Ward, *Anal. Chem.*, **37**, 268 (1965).
10) T. Fujiyama, J. Herrin, and B. L. Crawford, Jr., *Appl. Spectrosc.*, **24**, 9 (1970).
11) W. J. Potts, Jr., "Chemical Infrared Spectroscopy," Vol. 1, John Wiley & Sons, N.Y. (1963).
12) J. Koike, T. Suzuki, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **49**, 2724 (1976).
13) M. Kakimoto and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **48**, 2258; **49**, 3003 (1975).
14) T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **46**, 87 (1973). In this report, one of the present authors (TF) made a serious mistake. In the report, "the 367 cm^{-1} line of liquid chloroform" should be read "the 672 cm^{-1} line of liquid chloroform."
15) International Critical Tables, McGraw-Hill Book Company, Vol. III, N. Y. (1928), pp. 27ff.
16) G. Eckhardt and W. G. Wagner, *J. Mol. Spectrosc.*, **19**, 144 (1968).
17) Weissberger *et al.*, "Organic Solvents, Technique of Organic Chemistry," Interscience Publishers, N. Y. (1955), Vol. VII.
18) S. N. Ghosh, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **87**, 172 (1952); *J. Chem. Phys.*, **21**, 308 (1953).
19) C. P. Smyth and O. S. Morgan, *J. Am. Chem. Soc.*, **50**, 1547 (1928).