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Temperature Effect on Raman Intensity of Liquid Sample and Local Field Correction

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The relative intensities of the 996 cm^{-1} line of liquid benzene and the 367 cm^{-1} line of liquid chloroform were observed at various temperatures with a high accuracy. The apparent intensity change due to the temperature was explained completely in terms of the local field effect, the density change, and the statistical distribution. The validity of Eckardt's correction factor was strongly supported. In the case of liquid chloroform, an intensity change due to intermolecular interaction was observed after the elimination of the above three factors. The reliability of the relative intensity measurements of Raman lines was discussed.

The reliability of relative intensity measurements of Raman spectra has been greatly increased in the past few years by improvements in laser Raman spectrophotometers. Raman intensity measurements observe light energy scattered from a sample; therefore, they have a great advantage, in principle, over 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. Moreover, the handling of a sample is much easier in Raman than in infrared spectroscopy, especially when temperature-control is involved in the measurements. On the other hand, the reproducibility of successively-observed Raman intensities is often spoiled by casual changes in the experimental conditions; the setting of a sample cell, a slight deviation in optical alignment, the purity of the sample, the cleanness of the cell-window, and so on.

Paying careful attention to these factors, the intensities of the fundamental lines of liquid benzene and chloroform were measured. Liquid benzene was chosen because the intensity of the 996 cm^{-1} line is very strong and was expected to be observed with a high accuracy. Another reason for choosing that molecule was that the intensity change due to intermolecular interactions was expected to be very small in its system. In the case of liquid chloroform, strong intermolecular interaction was expected; therefore, the intensity change due to the temperature may exhibit different features from that of liquid benzene.

Experimental

The spectrometer used for the present work was designed and constructed by the authors.[12] The instrument is composed of a He-Ne gas laser source (NEC, GLG 108, 50 mW), a Spex 1401 double monochromator, a HTV R-376 photomultiplier (S-20 response), a handmade lock-in amplifier (375 cps), and a recorder.

The linearity of the whole system was carefully checked. First, the out-put current of the photomultiplier was plotted against the light energy. The linearity was perfect for the out-put from zero through 20 microampere, which was equivalent to an out-put voltage of 20 volts with $R_p = 1$ megaohm. Then, the linearity of the amplifier was tested using attenuator (0.1 — 120 db for each 0.1 db). Finally, the linearity of the whole system was checked by plotting the final recorder out-put voltage against the light-energy which passes through the entrance slit of the monochromator. The light-energy was attenuated by using neutral filters (Kenko, ND). From the standard errors estimated from the linear-fitting, the linearity of the whole system was ascertained to be less than 1 per cent of the full scale as long as the out-put voltage was less than 10 volts.

Special attention was paid to the temperature of the room so as to keep the out-put power of the laser source constant. The stability of the laser out-put during the individual spectral measurements was observed by monitoring the light energy

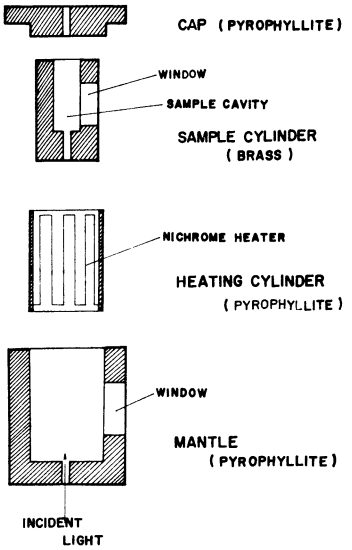

Fig. 1. Schematic Layout of High Temperature Cell.

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[1] K. S. Sehardi and R. N. Jones, *Spectrochim. Acta*, **19**, 1013 (1963).

[2] P. N. Schatz, *ibid.*, **21**, 617 (1965).

[3] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).

[4] H. E. Hallam, "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., *ibid.*, **72**, 2174 (1968).

[7] M. Yasumi, This Bulletin, **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. Spectry.*, **24**, 9 (1970).

[11] W. J. Potts, Jr., "Chemical Infrared Spectroscopy," Vol. 1, John Wiley and Sons, Inc., N. Y. (1963).

[12] T. Fujiyama and M. Tasumi, *Bunko Kenkyu*, **20**, 28 (1971).

which penetrated through the 100 per cent reflectance mirror of the laser cavity. When the power of the laser source drifted more than 1 per cent during the measurements, the data observed were completely discarded.

The high-temperature cell used for the measurements is illustrated in Fig. 1. It is mainly made of *pyrophyllite*, which is easy to shape and which is a good thermal insulator. Brass was used for the sample cylinder of Fig. 1 so as to obtain a homogeneous temperature atmosphere inside the cylinder, in which a sample cell (a 10×10×15 mm cube) was placed. The temperature was controlled by changing the electric current supplied to the nichrome heater. The temperature was observed by means of a thermocouple directly inserted into the samples. The accuracy of the temperature measurements was believed to be within ±1°C.

The benzene and chloroform used for the measurements were commercial products and were used for the measurements just after fractional distillation. The purity of the samples was checked by the use of gas chromatography.

Results and Discussions

996 cm^{-1} Line of Benzene. The Raman intensity of the 996 cm^{-1} line of liquid benzene was observed in the temperature range from 24 through 70°C. The intensity was determined from the band area by the weight-method. The averaged value of the five intensity data was taken as the observed Raman intensity; it had a standard deviation of from 0.3 to 0.6 per cent. The observed relative intensity ratios are summarized in Table 1, where the relative intensity at 24°C is chosen as the standard. The relative error of the individual ratio is estimated to be ±1 per cent. Obviously, the relative intensity decreases more than 10 per cent as the temperature changes from 24 to 70°C. The results are also illustrated in Fig. 2.

TABLE 1. INTENSITY CHANGE OF THE 996 cm^{-1} LINE OF BENZENE

t(°C)	L/L_{24}	s/s_{24}	d/d_{24}	Lsd/Lsd_{24}	I/I_{24}
24	1.000	1.000	1.000	1.000	1.000
36	0.979	1.002	0.986	0.967	0.960
47	0.959	1.002	0.972	0.934	0.930
58	0.939	1.005	0.958	0.905	0.912
70	0.918	1.007	0.943	0.872	0.891

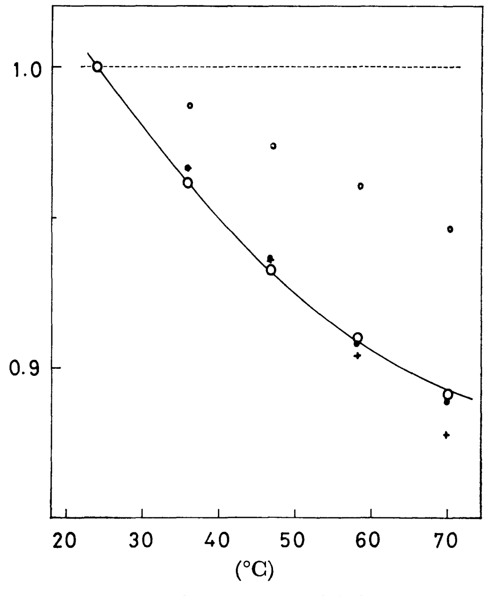

Fig. 2. Comparison of I/I_{24} and Lsd/Lsd_{24}
○: I/I_{24}, ○: d/d_{24}, +: Ld/Ld_{24}, ●: Lsd/Lsd_{24}

The apparent intensity change due to the temperature has been discussed by Person[13] for the infrared absorption case, where the importance of the local-field correction has been emphasized. For the case of Raman intensity, various authors have proposed correction factors to the local field that allow Placzek's intensity formula to be applied to liquids and/or solutions.[14–19] In addition to the local-field effect, the density change and the statistical distribution of molecules in relation to a vibrational state may contribute to the change in the apparent Raman intensity due to the temperature. 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.[20] The relative values of the density at various temperatures are summarized in Table 1, where the density at 24°C is chosen as a standard.

The statistical factor, s, may be expressed as:

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

where ν is the frequency displacement of a Raman line from that of the incident wave, T is the temperature, h is the Planck's constant, k is the Boltzmann constant, and c is the velocity of light. The calculated relative values of s are summarized in Table 1, where the s-value at 24°C is taken as a standard. The contribution of s to the change in the intensity is much smaller than the experimental error.

Eckardt[18] emphasized that the most appropriate factor for the local-field correction in Raman scattering, L, is:

$$L = (n_s/n_0)(n_s^2+2)^2(n_0^2+2)^2/81$$

where n_s is the refractive index at the Stokes frequency and where n_0 is the index at the frequency of the incident light. If the variation in the refractive index over the frequency range of the Raman shift is ignored, the equation reduces to:

$$L = \frac{(n^2+2)^4}{81}.$$

The calculated relative values of the local-field correction factor, L/L_{24}, are summarized in Table 1. Again, L at 24°C is taken as the standard. In the calculation, the refractive indices for different temperatures were

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13) W. B. Person, *J. Chem. Phys.*, **28**, 319 (1958).

14) W. C. Mallard and J. W. Straley, *ibid.*, **27**, 877 (1957).

15) V. M. Pivovarov, *Opt. Spectrosc.*, **9**, 139 (1960).

16) G. Fini, P. Mirone, and P. Patella, *J. Mol. Spectrosc.*, **28**, 144 (1968).

17) P. Mirone, *Spectrochim. Acta*, **22**, 1897 (1966).

18) G. Eckhardt and W. G. Wagner, *J. Mol. Spectrosc.*, **19**, 407 (1966).

19) N. K. Sidorov, L. S. Stalmakhova, and N. V. Bogachyov, *Opt. Spectrosc.*, **30**, 375 (1971).

20) International Critical Tables, McGraw-Hill Book Company, Inc., N. Y., (1928), Vol. III, pp. 27ff.

estimated from the empirical Eykman equation:

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

where C is a constant characteristic for a molecule; M, the molecular weight, and d, the density.[21]

Finally, the products of L, s, and d were calculated; they are summarized in Table 1 (designated as (Lsd)). The relative values, $(Lsd)/(Lsd)_{24}$, are expected to agree with those of the relative intensity, I/I_{24}, if the factors considered here mainly contribute to the apparent intensity change due to the change in temperature. Actually, the agreement between these two sets of values is excellent. In Fig. 2, the observed relative intensities are compared with those corrected for these three factors, L, s, and d.

TABLE 2. INTENSITY CHANGE OF THE 367 cm^{-1} LINE OF CHLOROFORM

t(°C)	L/L_{24}	s/s_{24}	d/d_{24}	Lsd/Lsd_{24}	I/I_{24}
24	1.000	1.000	1.000	1.000	1.000
35	0.981	1.002	0.986	0.970	0.866
40	0.957	1.003	0.980	0.941	0.815

367 cm^{-1} Line of Chloroform. Exactly the same procedures were applied to the 367 cm^{-1} line of liquid chloroform. The results are summarized in Table 2. It can be seen in the table that the relative intensity of the 367 cm^{-1} line decreases more than 20 per cent as the temperature changes from 24 to 40°C, while the calculated correction factor, $(Lsd)/(Lsd)_{24}$, decreases only 6 per cents. The discrepancy between the observed and the calculated intensity ratios corresponds to the real change in the intensity of the line on passing from 24 to 40°C; this can be explained with respect to the intermolecular interactions, such as the break-down of hydrogen bonding between chloroform molecules in the liquid phase on the elevating of the temperature. The details will be discussed elsewhere, together with the intensity change in the absorption spectra.

Local-field Correction and Conclusion. A few important conclusions can be drawn from the present results. The intensity change in the 992 cm^{-1} Raman line of liquid benzene can be completely explained by L, s, and d; that is, the Raman scattering cross section per molecule does not change when the temperature varies. Among the three factors, the local-field correction is the main factor changing the apparent intensity. Eckardt's formula is based upon these ideas: (1) the Lorentz-field consideration is applicable to the system, and (2) the scattering may be thought of as the absorption of a light quantum, followed by the emission of another quantum; therefore, the local-field correction for the scattering is the product of the local-field corrections for absorption and for spontaneous emission.[22,23] Therefore, the effect of the local field on the apparent intensity is much greater for the Raman than for the infrared absorption intensity. In the latter case, L is expressed as:

$$L = \frac{(n^2+2)^2}{9}$$

assuming the Lorentzfield.[3] It can easily be ascertained that the intensity change due to temperature variation cannot be explained by this formula, which means that the present results strongly support the assumption (2) of Eckardt and contradicts the propositions of the references.[14,15] It may also be concluded from the present results that the choice of the Lorentzfield for the liquid benzene is reasonable.

The other important conclusion drawn from the present result is that the L and d factors do not depend upon the frequency, ν; this means that the apparent intensity change due to the change in temperature is the same magnitude for all the Raman-shift region. Therefore, the factors do not contribute to the observed relative intensities of Raman lines with different frequencies. In the preceding discussions, the refractive index of a sample was assumed to take a constant value for all the frequency range under consideration. In a case where a sample is absorbing, *e.g.*, the case of a resonance Raman, the refractive index value changes considerably over the Raman-shift range. Therefore, the consideration of the local-field effect is extremely important.

Incidentally, it may be concluded that the measurements of the relative intensities of Raman lines are much easier and more reliable than those of the infrared absorption in the sense that the observed data are nearly free from any systematic errors which spoil the reliability of the relative intensities.

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[21] Weissberger *et al.*, "Organic Solvents," Techinique of Organic Chemistry, Interscience Publishers, Inc., N. Y., 1955, Vol. VII.

[22] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, *Phys. Rev.*, **127**, 1918 (1962).

[23] P. D. Maker and R. W. Terhune, *ibid.*, **137**, A801 (1965)·