BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(8), 2385—2386 (1975)

Energy Difference between Rotational Isomers of 1,2-Dibromoethane

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(Received March 27, 1975)

Synopsis. The energy difference between the rotational isomers of 1,2-dibromoethane in the liquid state was determined to be 910±80 cal/mol on the basis of the relative intensity of the Raman band at 660 cm^{-1} (*trans* form) to that at 551 cm^{-1} (*gauche* form) in the temperature range from 24.5 to 105.1 °C.

The energy difference ($\varDelta E=E_g-E_t$) between the *trans* and *gauche* forms of 1,2-dibromoethane in the liquid state has been determined by many investigators.[1–7] The values reported are in the range from 650 to 1000 cal/mol. Fujiyama and Shimanouchi observed the ratio of the intensity of the Raman band at 660 cm^{-1} of the *trans* form (I_t) and that of the band at 551 cm^{-1} of the *gauche* form (I_g) in the liquid state and concluded that $\ln(I_t/I_g)$ was not proportional to $1/T$ (T represents the absolute temperature at the measurement).[5] Recently a cryostat was constructed in our laboratory for the measurement of the Raman spectra in the temperature range from 150 °C to liquid helium temperature.[8] By use of the apparatus we re-examined the energy difference of 1,2-dibromoethane in the liquid state in order to ascertain the non-linear relation between $\ln(I_t/I_g)$ and $1/T$.

The Raman spectra were measured with the use of a Raman spectrometer, Kawaguchi Electric Works Ltd. model RL-62. The exciting light was 488.0 nm line of the Ar^+ laser, NEC model GLG 2003. The power of the exciting light was kept constant during the measurement by use of the light feed back system for the GLG 2003 laser made by Kawaguchi Electric Works Ltd. The spectrum between 500 and 750 cm^{-1} was recorded at 24.5, 34.9, 45.0, 55.2, 65.0, 75.2, 84.9, 95.1, and 105.1 °C. The spectrum at room temperature is given in Fig. 1. The weak band at 583 cm^{-1} is the CBr stretching vibration band of b species of the *gauche* form. The bands at 660 and 551 cm^{-1} were used for obtaining the energy difference. The temperature was measured within an accuracy of about 0.03 K with the use of a chlomel p-constantan thermocouple, the calibration of which was given elsewhere.[9] The drift of the temperature was less than 0.2 K during a measurement. The spectra were recorded five times for the measurement at each temperature. Five copies were made for each recording with the use of Fuji Xerox 1000 and weighed the area of each band. 25 data of I_t/I_g were obtained for the measurement at each temperature. The standard deviation of the 25 data was in the range from 1.0 to 3.5% of the averaged value.

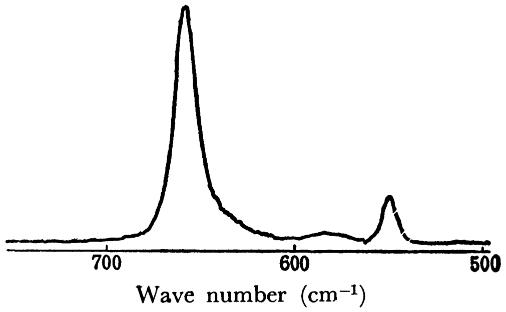

Fig. 1. The Raman spectra of 1,2-dibromoethane in the liquid state at room temperature.

Figure 2 illustrates the values of $\ln(I_t/I_g)$ against $1/T$, which indicates that $\ln(I_t/I_g)$ linearly depends on $1/T$. As the scattering intensity of the Stokes line[10] is proportional to $(1-e^{-h\nu/kT})^{-1}$, the temperature dependence of I_t/I_g can be expressed by the following equations:

$$\partial/\partial(1/T)[\ln(I_t/I_g)] = \varDelta E/k + f(T)$$

$$f(T) = e^{-h\nu_g/kT}(h\nu_g/k)/(1-e^{-h\nu_g/kT}) - e^{-h\nu_t/kT}(h\nu_t/k)/(1-e^{-h\nu_t/kT})$$

where ν_t and ν_g represent the vibrational frequencies of the *trans* and *gauche* forms used for the determination of $\varDelta E$. The apparent value of $\varDelta E$ directly obtained from Fig. 2 is 955±80 cal/mol. When $f(T)$ is taken into consideration, the value of $\varDelta E$ decreases by 38 cal/mol at 24.5 °C and by 54 cal/mol at 105.1 °C. Consequently, the value of $\varDelta E$ is determined to be 910±80 cal/mol.

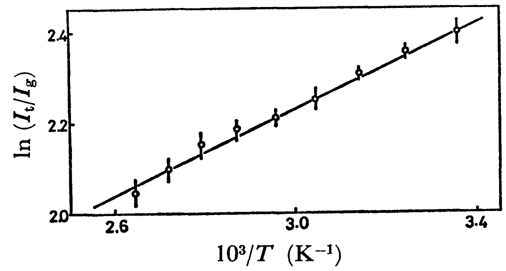

Fig. 2. Linearity between $\ln(I_t/I_g)$ and $1/T$.

As temperature range of the present study is wider and the measurement of temperature is more accurate than other vibrational spectroscopic measurements, we believe the present result is most reliable among them. I_t/I_g depends on the choice of the base line and also on the method of the separation of two bands ovelapping each other. As Fig. 1 shows, the two bands do not overlap each other so much and the base line is easily determined in this case. On estimating the error in I_t/I_g in Fig. 2, such systematic errors are not taken into account, which do not exceed 5%.

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