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Raman Spectra and Internal Rotation of Ethyl Methyl Ether

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The Raman spectra of ethyl methyl ether in the liquid state were measured at various temperatures from 298 K to 195 K. The energy difference between the *gauche* and *trans* isomers in the liquid state was found to be 1.1 kcal/mol. This value is appreciably higher than the value 0.77 kcal/mol for *n*-butane. The tendency of assuming the *trans* form is higher for the CH_2–O bond than for the CH_2–CH_2 bond. The infrared intensity of the band at 465 cm^{-1} (gas) is largely due to the *gauche* isomer but the Raman intensity of the line at 471 cm^{-1} (liquid) is largely due to the *trans* isomer.

The infrared and Raman spectra of ethyl methyl ether in the gaseous, liquid, and crystalline states have been analyzed[1-8] and it has been established that the *trans* and *gauche* isomers coexist in the gaseous and liquid states while only the *trans* isomer remains in the crystalline state. Vibrational assignments of low frequency vibrations have been established, including internal-rotation vibrations of the methyl groups and the threefold potential barriers of the methyl groups of the *trans* isomer have been studied.[7,8]

Energy-difference data of rotational isomers about CH_2–O bonds are important for studying internal-rotation of polyethers including polyethylene glycol. The energy difference between the *gauche* and *trans* isomers of ethyl methyl ether in the gaseous state has been obtained as $\Delta H(H_g - H_t) = 1.5 \pm 0.2$ kcal/mol[4] from the temperature dependence of the relative intensity of the infrared bands at 375 cm^{-1} (*gauche*) and at 280 cm^{-1} (*trans*). On the other hand, the energy difference in the dilute carbon-disulfide solution has been determined as 1.35 kcal/mol[7] from the relative intensity of the infrared bands at 980 cm^{-1} (*gauche*) and at 1015 cm^{-1} (*trans*).

For measuring infrared intensities in the low-frequency region, it is required to take due care of natural emission from the sample and/or the attenuator of a double-beam spectrophotometer. Thus, corrections were made[4] for natural emission from the gas cell at elevated temperatures and relative intensities of the infrared bands of rotational isomers were measured. On the other hand, in measuring absorption intensities of the sample in a low-temperature cell, the natural emission from the optical attenuator causes a systematic error. Apparent transmittance of infrared bands is shifted lower than actual transmittance, unless the double-chopping method is used.[8]

Intensity measurements of Raman lines are not disturbed by these systematic errors, and more reliable values of energy differences may be obtained. In the present study, the Raman spectra of ethyl methyl ether in the liquid state at low temperatures were measured in order to determine the energy difference in the liquid state.

Experimental

The sample of ethyl methyl ether (b.p. 279 K) as prepared in the preceeding study[8] was transferred through a vacuum

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line and was sealed into a liquid cell. The liquid cell was then held in a low-temperature apparatus. Raman spectra were excited with an argon-ion laser (488.0 nm) and were measured with a JEOL Raman spectrometer (Model JRS-02AS).

Results

Relative intensities of Raman lines of ethyl methyl ether in the liquid state were found to vary markedly with temperature. Typical examples of the Raman spectra at 298 K and 200 K are shown in Fig. 1. Thus, the relative intensities of the Raman lines at 381, 978, and 1069 cm^{-1} were found to be stronger at higher temperature than at lower temperature. These Raman lines correspond to the infrared bands at 376 cm^{-1} (in CCl_4 solution[4]), 979 and 1068 cm^{-1} (in CS_2 solution[6]) which are not observed in the crystalline state and accordingly are assigned to the *gauche* isomer. The Raman lines due to the *trans* isomers are observed at 471, 1015, and 1120 cm^{-1}.

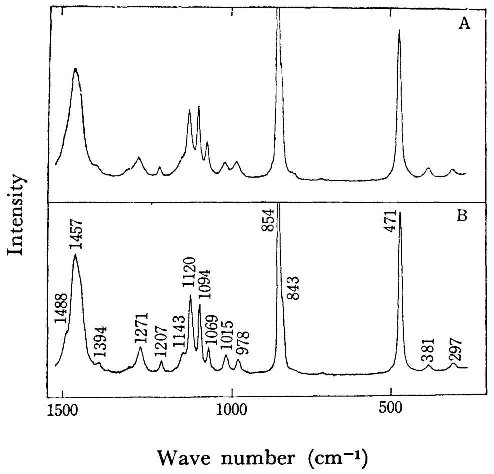

Fig. 1. Raman spectra of ethyl methyl ether in the liquid state, (A) at 298 K and (B) at 200 K, excitcd with an argon-ion laser (488.0 nm).

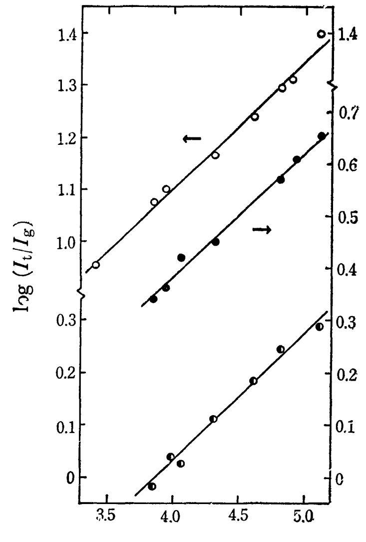

Fig. 2. Temperature dependence of the intensity ratios of the Raman lines of the *trans* isomer (I_t) and the *gauche* isomer (I_g), ○: 471 cm^{-1}/381 cm^{-1}, ◐: 1015 cm^{-1}/978 cm^{-1}, ●: 1120 cm^{-1}/1069 cm^{-1}.

The ratios of area intensities of the Raman lines of the *gauche* (I_g) and *trans* isomers (I_t) were measured at temperatures from 298 K to 195 K (Fig. 2). The energy difference $[\Delta H(H_g-H_t)]$ between the *gauche* and *trans* isomers was found to be 1.1±0.1, 1.1±0.2, and 1.1±0.1 kcal/mol from the pairs (*trans*/*gauche*) of Raman lines [471 cm^{-1}/381 cm^{-1}], [1015 cm^{-1}/978 cm^{-1}], and [1120 cm^{-1}/1069 cm^{-1}], respectively. Thus the values of ΔH obtained from the three pairs agreed closely with one another.

For the pair of the Raman lines at 1094 cm^{-1}/1069 cm^{-1}, the apparent energy difference was obtained as 0.9±0.1 kcal/mol. This value is slightly smaller than the value of $\Delta H(H_g-H_t)=1.1$ kcal/mol, so that the Raman intensity at 1094 cm^{-1} is largely due to the *trans* isomer but also partly due to the *gauche* isomer.

Discussion

The energy difference $\Delta H=1.1$ kcal/mol in the liquid state is smaller than the value $\Delta H=1.35$ kcal/mol in CS_2 solution[7] or the value $\Delta H=1.5$ kcal/mole in the gaseous state.[8] The small difference between the values in the liquid state and in the gaseous state is due to the small difference between the dipole moments of the *trans* and *gauche* isomers.

The energy difference $\Delta H=1.1$ kcal/mol for ethyl methyl ether [CH_3–CH_2–O–CH_3] in the liquid state is appreciably higher than the value $\Delta H=0.77$ kcal/mol for *n*-butane [CH_3–CH_2–CH_2–CH_3].[9] This indicates that the tendency of assuming the *trans* form is higher for the CH_2–O bond than for the CH_2–CH_2 bond. Similarly, the energy difference [$\Delta H=1.1$ kcal/mol[10] or 1.37 kcal/mol[11]] between the *trans-gauche* and *trans-trans* isomers of diethyl ether [CH_3–CH_2–O–CH_2–CH_3] is appreciably higher than the value $\Delta H=0.60$ kcal/mol[12] for *n*-pentane [CH_3–CH_2–CH_2–CH_2–CH_3].

The relative intensity of the infrared bands of the gaseous state at 375 cm^{-1} (*gauche*) and 465 cm^{-1} was previously[8] found to be independent of temperature indicating that the bands of the *trans* and *gauche* isomers overlap at 465 cm^{-1} and the intensity of the composite band is largely due to the *gauche* isomer. However, in the Raman scattering, the relative intensity of the Raman lines at 1120 cm^{-1} (*trans*) and 471 cm^{-1} (in the liquid state) is independent of temperature so that the Raman scattering intensity at 471 cm^{-1} is almost exclusively due to the *trans* isomer. For the *trans* isomer of ethyl methyl ether, the Raman line at 471 cm^{-1} corresponds to the Raman line of liquid *n*-butane at 425 cm^{-1} and is assigned to the accordion vibration. On the other hand, the antisymmetric C–C–C–C deforma-

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tion frequency of the *gauche* isomer of *n*-butane is calculated very close to the accordion frequency of the *trans* isomer13) but has not been observed separately in the Raman scattering. Similarly, the Raman intensity of the 'antisymmetric' C–C–O–C deformation vibration of the *gauche* isomer of ethyl methyl ether may well be negligible as compared with the Raman intensity of the accordion vibration of the *trans* isomer.

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