

Energy Difference between Rotational Isomers of Methyl Ethyl Ether

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Raman lines due to skeletal bending modes of methyl ethyl ether were observed at 381 (weak) and 471 cm^{-1} (strong) for the liquid phase.¹⁻³⁾ Corresponding infrared bands were observed at 370 and 464 cm^{-1} for the vapor phase at room temperature.^{2,3)} However, the band at 370 cm^{-1} was not observed in the solid state and was assigned to the gauche isomer, whereas the band of the solid phase at 472 cm^{-1} was assigned to the trans isomer.⁴⁾ The molecular structure of the trans isomer was determined by microwave analysis.⁵⁾ Measurement of the energy difference between the rotational isomers of methyl ethyl ether is also important for studying conformations of polymers, *e.g.*, polyethyleneglycol⁶⁾ in solution.

In the present study, the infrared spectra of methyl ethyl ether in the gaseous, liquid and solid states were measured in the region 550–200 cm^{-1} . The length of the gas cell used was 105 mm and the sample pressure was 660 mmHg at 303°K. The liquid cell (about 0.2 mm thick) was connected to a vacuum line and was kept at 204°K. The ether sample was distilled into the cell. For preparing a solid film, vapor was condensed on a cesium iodide window at 98°K and the solid was then annealed at 145°K. Typical spectra of the vapor, liquid, and solid phases are shown in Fig. 1. Temperature dependence of the intensities of liquid bands was observed and the bands at 258 and 300 cm^{-1} were found to become stronger as temperature was lowered. Accordingly, the area intensities of

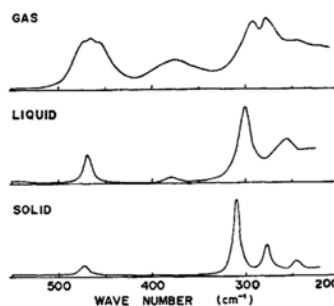


Fig. 1. Infrared absorption (optical density) curves of methyl ethyl ether.

the bands at 380 cm^{-1} (gauche) and 300 cm^{-1} (trans) were measured at 259, 248, 237, 228, 223, 216, 210, 204, and 198°K, and the energy difference between the rotational isomers was found as $\Delta H = H(\text{gauche}) - H(\text{trans}) = 1.5 \pm 0.1$ kcal/mol for the liquid phase. Temperature dependence of the vapor bands at 465, 375, and 280 cm^{-1} was also observed. After making corrections for emission from the cell at elevated temperatures, area-intensity ratios were measured at 303, 333, 375, and 423°K and the energy difference was found as $\Delta H = 1.5 \pm 0.2$ kcal/mol for the vapor phase. (From this value, the population of the gauche isomer is calculated to be as small as ~5% at ~200°K where microwave absorption lines of the gauche isomer were not identified.⁵⁾) Thus, the ΔH values for the vapor and liquid phases of methyl ethyl ether are like, as expected from small dipole-moment difference between the two isomers.

The band of the liquid and vapor phase at ~465 cm^{-1} was previously assigned to the trans isomer, because the corresponding band was also observed in the solid phase. However, apparent relative intensities of the bands at 375 cm^{-1} (gauche) and 465 cm^{-1} were 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.

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