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Vibrational Spectroscopy 15 (1997) 211–218

VIBRATIONAL SPECTROSCOPY

Infrared spectra and spinning diffusion of methyl bromide in solutions

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Received 7 February 1997; accepted 21 June 1997

Abstract

Infrared absorption spectra of methyl bromide (CH_3Br) dissolved in carbon tetrachloride (CCl_4) and carbon disulfide have being studied in wide temperature ranges. IR absorption in the regions of degenerate (E-type) bands belonging to CH_3-stretching (ν_4) and deformational (ν_5, ν_6) vibrations were fitted by the sum of Cauchy–Gauss components. Each E-type band was reproduced by the two components: the narrower (n) and the broader (b) one. The narrower components of the bands belonging to deformational CH_3-vibrations were interpreted within the framework of the orientational diffusion mechanism. The broader components of these bands were attributed to the unresolved gas-like vibration–rotational absorption of the molecules. The different temperature behaviour of the components has been found: the integrated intensities of the narrower components (I_n) decrease with temperature, while the intensities of the broader ones (I_b) increase. The enthalpy differences between the molecules absorbing via two different mechanisms (ΔH) were determined from the dependencies of $ln(I_n/I_b)$ upon T^{-1}: 0.87 ± 0.28 (ν_5) and 0.65 ± 0.10 kcal mol^{-1} (ν_6). These values are close to those determined previously for CH_3I and CD_3I. The narrower components' band widths were used for evaluating the spinning diffusion constants for CH_3Br in solutions. © 1997 Elsevier Science B.V.

Keywords: Orientational diffusion; Free rotation; Methyl bromide; Vibrational relaxation; Infrared spectra

1. Introduction

Orientational dynamics of the molecules having the general formula CH_3X (X=F, Cl, Br, I, C≡N) is an object of extensive study. All these molecules are symmetric tops having essentially different moments of inertia for spinning (rotations of the symmetry axis, ∥) and tumbling (rotation of the symmetry axis, ⊥) motions. The most part of the documented data has been obtained for two representativeness of the CH_3X series: methyl iodide and acetonitrile (see, for example [1–4] and references cited therein). In the present work we make an attempt to investigate the dynamics of spinning motion of methyl bromide (CH_3Br) in condensed phase. There were several studies of the tumbling motion of this molecule in the liquid phase [5,6], however, up to our knowledge, its spinning diffusion has not been studied so far.

Normal vibrations of the CH_3X-type molecules (which refer to the C_{3V} point symmetry group) are subdivided into symmetric (A_1-type) and double de-

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PII S0924-2031(97)00030-1