

CONFORMATIONAL ANALYSIS OF A SERIES OF $\text{CH}_3\text{MH}_2\text{OM}'\text{H}_2\text{CH}_3$ (M, M' = C AND Si) BY RAMAN SPECTROSCOPY AND DENSITY FUNCTIONAL THEORY

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Abstract: Raman spectra in the liquid and solid states for a series of diethyl ether and its organosilicon derivatives, $\text{CH}_3\text{MH}_2\text{OM}'\text{H}_2\text{CH}_3$ (M, M' = C and Si), were measured. Normal vibrations of these molecules were assigned by using density functional theory with the B3LYP/6-31G* and B3LYP/6-311+G** methods. Stable molecular forms in the liquid and solid states have been discussed.

Vibrational spectroscopy is a powerful technique to obtain information on various structural properties of molecules, and normal coordinate analysis of molecules is useful for the assignments of the spectra. Normal coordinate analysis by empirical force field calculation was, however, rather complicated for large molecules. In recent years, theoretical calculations by density functional theory (DFT) have afforded accurate vibrational wavenumbers for many molecules.

A number of interests have been focused on the conformational stability of diethyl ether (DEE) in previous experimental and theoretical studies [1–11]. Although, a molecule of DEE has nine possible rotational isomers with respect to the two skeletal axes, the number of independent isomers is reduced, owing to the existence of mirror image isomers, to four, *TT*, *TG*, *GG* and *GG'*, where the first and second symbols designate the conformations (*T*: *trans*; *G*: *gauche*) about the $(\text{CH}_3)\text{CH}_2\text{--O}(\text{CH}_2)$ and $(\text{CH}_2)\text{O--CH}_2(\text{CH}_3)$ axes, respectively. The previous experimental studies of DEE showed that only the *TT* and *TG* forms exist in the gaseous and liquid states and the *TT* form exists in the solid state [1–5].

In the case of bis(methylsilyl) ether, $\text{CH}_3\text{SiH}_2\text{OSiH}_2\text{CH}_3$ (BMSE), Rankin and Robertson [12] showed in their electron diffraction work the molecular forms that exist in the gaseous state. They concluded that BMSE has at least two forms in the gaseous state, the major one (64%) having the methyl groups by 124° and 58° (*SG* form; *S*: *skew*) away from the positions at which the Si–C bonds are *T* to the O–Si bonds. There are, however, no conformational studies in the liquid or solid states. For ethyl methylsilyl ether, $\text{CH}_3\text{CH}_2\text{OSiH}_2\text{CH}_3$ (EMSE), no vibrational spectroscopic studies have been reported.

In this study, we report the conformational stability of a series of DEE, EMSE and BMSE systematically using Raman spectroscopy and DFT calculations in order to obtain information on the conformational stability around the C–O and Si–O bonds.

The DFT calculations by the B3LYP/6-31G* and 6-311+G** methods were carried out by using the Gaussian 98 program. The initial structural parameters for geometry optimization were taken from those reported for DEE [10] and BMSE [12]. The calculated relative molecular energies and the populations at 298 K for the optimized forms are listed in Table 1.

For DEE, Kuze et al. [10] have reported the stable molecular forms as determined by electron diffraction and microwave spectroscopy and the geometry optimization at the HF/4-31G level; only the *TT* and *TG* forms exist in the gaseous state, the population of the *TT* form being 69% at 300 K. The results of the present DFT calculations support their results (Table 1). The populations of the *GG* and *GG'* forms are negligibly small and the *TT* and *TG* forms are found to be stable in the gaseous state.

Table 1. Relative energies and populations for the molecular forms of DEE, EMSE and BMSE

molecular form	DEE		EMSE		BMSE	
	rel. energy ¹⁾	population ²⁾	rel. energy ¹⁾	population ²⁾	rel. energy ¹⁾	population ²⁾
<i>TT</i>	0.000	0.762	0.000	0.466	0.000	0.368
<i>TG</i>	1.539	0.226	0.734	0.269	-	-
<i>GT</i>	-	-	0.744	0.265	-	-
<i>GG</i>	2.987	0.010	-	-	-	-
<i>GG'</i>	3.873	0.002	-	-	-	-
<i>SS</i>	-	-	-	-	0.091	0.632

¹⁾ Relative energies from the calculation using the B3LYP/6-311+G** method.

²⁾ Population at 298 K.

For EMSE, there may be five possible forms with an additional *GT* form. Since the structural optimization of the *GG* and *GG'* forms resulted in the *TG* form (Table 1), the observed Raman wavenumbers were compared only with the calculated results for the *TT*, *TG* and *GT* forms. Figure 1 shows the Raman spectra of EMSE-*d*₂ in the liquid and solid states and the results of the DFT calculations, indicating that the *TT*, *TG* and *GT* forms coexist in the liquid state and only the *TT* form exists in the solid state.

For BMSE, the results of the geometry optimization showed that the *GG'* form was converted to the *TT* form and the *GT* and *GG* forms to the *SS* form (Table 1). The *SG* form reported [12] was optimized, as it is, into the *SG*. However, the higher-level B3LYP/6-311++G** method yielded the *SS* form for this.

Normal coordinate analysis for the three molecules was also conducted by using the revised NCTB program [13] to work out the potential energy-distributions in terms of the group coordinates.

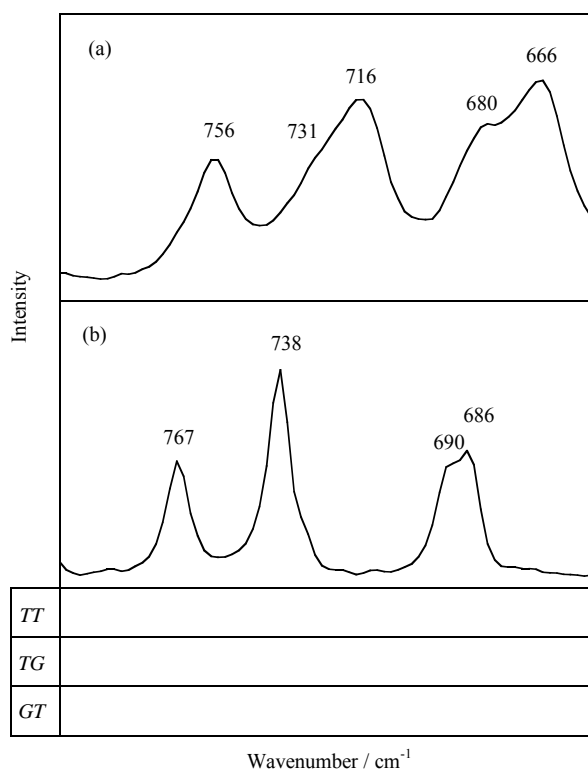


Fig. 1. Raman spectra (800-650 cm⁻¹) of EMSE-*d*₂ and the calculated wavenumbers for possible molecular forms: (a) liquid state at room temperature and (b) solid state at liquid nitrogen temperature.

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