



The structural configurations of Ethylene Trithiocarbonate in the binary mixture ($\text{SCS}_2\text{CH}_2\text{CH}_2 + \text{CHCl}_3$) investigated by polarized Raman: Experimental and quantum chemical results



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ABSTRACT

The isotropic and anisotropic components of the Raman spectra of C=S stretching in Ethylene Trithiocarbonate ($\text{SCS}_2\text{CH}_2\text{CH}_2$, ET) shows noncoincidence effect (NCE). The calculated absolute Raman cross-section (ARCS) of C=S stretching initially increases with the dilution of concentration to a maximum and then decreases. This unusual behavior indicates the existence of self-association. Thus we proposed aggregated model and the dimer structure were optimized with DFT/PCM to explain the NCE and ARCS behaviors. Vibrational spectra and depolarization-ratio were calculated for monomer and dimer individually, the dimer is in good accordance with the experimental data. The strong antiparallel C=S vibrational coupling in neighboring molecules accounts for the frequency shifts of the C=S stretching.

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1. Introduction

As is known to all, intermolecular vibrational coupling is widely research areas which play important roles to understanding structure and properties of matter and processes in physics chemistry and biology, So many experimenters and theorists have paid their attention to these fields [1–10]. Intermolecular vibrational coupling is mainly caused by the transition dipole coupling between the vibrations of different molecules [11,12]. In order to better analyze vibrational coupling between different molecules in liquid phase systems, the prerequisite is to properly understand the influences of neighboring molecules, those effects come from two streams [4,6], diagonal effect and off-diagonal effect. Diagonal effect refers to the surrounding environment that influence on a vibration mode. It is also to say “solvent effect”. This effect is largely affected by the concentration and solvent property. The off-diagonal effect is the direct vibrational coupling between molecules, this effect will inevitably lead to those resonant vibrational modes in spatial delocalization [4] and consequently give rise to

vibrational frequencies shift, which is termed as noncoincidence effect (NCE) [13,14]. The NCE denote the phenomenon that the isotropic and anisotropic components of the Raman bands as well as the infrared (IR) band of the same vibrational mode appear at different wavenumber positions. The NCE [13,14] value is defined as $\Delta\nu_{\text{NCE}} = \nu_{\text{aniso}} - \nu_{\text{iso}}$. The NCE is considered as an efficient spectral probe to investigate the local conformation transition and to follow structural changes that occur during the polarity transition in physiological activity, and has been studied extensively through the experiment, computing simulation and theoretical model methods [1,3,5,7,12,15–18]. The NCE of C=O, C–O, OH, and S=O stretching modes and NH_2 bending modes in the binary liquids have been reported by experiment or MC or MD simulation [18] and explained by Logan’s model or Mirones’s model [3,15]. The NCE value shows positive in most cases, but also sometimes shows negative depending on the orientation of the coupling dipoles [15,19].

Recently the C=S stretching mode in ethylene trithiocarbonate (ET) have been reported to have the NCE phenomenon [20]. It was found that the calculated absolute Raman cross section of C=S stretching increases distinctly when the ET is diluted, this unusual behavior may predicate the occurrence of new species such as dimers or high-degree self-association form. Additionally, traditional theory believe that molecular dipoles organized in a short or long-

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range orientational order accounts for the appearance of NCE phenomenon [3,15–19], the short-range orientational order organization could be calculated with DFT [21–24]. In this article we apply DFT/PCM (polarizable continuum model) calculation for interpretation of ET NCE phenomenon with optimized ET dimer structure.

2. Experimental and computational methods

The reagent: Ethylene Trithiocarbonate ($\text{SCS}_2\text{CH}_2\text{CH}_2$, TCL, >99.0%); chloroform (AR, *shanghai San Ying* chemical reagent company) The Raman spectra were obtained by exciting the sample with the 488 nm line emitted from an Ar ion laser (Coherent, CVI MELLES GRIOT), collecting the scattered light by the use of a triple monochromator (TriVista TR557, Princeton Instruments) equipped with a liquid nitrogen cooled CCD array (manufacturer, Princeton Instruments Inc; model ID:LN/2048X512.B/I,UVAR.). The experimental setup has the wave number coverage of 1089 cm^{-1} (488 nm laser) and a spectral resolution of 2.5 cm^{-1} . In the spectroscopic range of interest the pixel separation amounts to 0.5 cm^{-1} . A polarization scrambler was placed between the polarizer and the spectrometer entrance slit. All measurements were carried out at room temperature (293 K) and atmospheric pressure. Of all the running, the same integration time of 200 s and the same accumulations number [20] been taken for all different concentrations to obtain high quality of signal/noise ratio in all experiments. The spectral intensity of each mixture was constantly checked against that of the neat liquid normal species.

Computational chemists often give attention to the specific technologies associated with computer memory, data, storage, processor speed, and program development software and can help to better understand the photophysical and photochemical characteristics of the molecule, Herein, density functional (DFT) calculations and the polarizable continuum model (PCM) were used to study the vibration frequency of ET in CHCl_3 , and its linear dimer at the B3LYP levels of theory with the 6-311G (d,p) basis set by using the Gaussian 09 program [25–27]. The solvent influence was included using the PCM, and the optimized geometry and the corresponding vibrational frequencies were obtained to verify the reasonable of dimer structure.

The polarized and depolarized Raman spectra of S=O stretching mode of ET were recorded in CHCl_3 solvent with the different variety of concentrations. The absolute Raman cross sections of ET were calculated from the intensity relative to the 668 cm^{-1} Raman band of the solvent CHCl_3 in the different concentrations. Meanwhile, the 668 cm^{-1} absolute Raman cross sections of CHCl_3 is deduced from the absolute Raman cross sections known CH_3CN . By collecting the Raman spectra of the equal volume mixture of CHCl_3 and CH_3CN , the absolute Raman cross sections of the 668 cm^{-1} Raman band of the CHCl_3 can be calculated the intensity relative to the 918 cm^{-1} Raman band of the CH_3CN . The detailed formula of the absolute Raman cross sections is $\sigma_N = \sigma_S(I_N/I_S)[(\nu_0 - \nu_S)/(\nu_0 - \nu_N)]^4(C_S/C_N)$ where σ_N and σ_S are the absolute Raman cross sections of the band being determined and of the internal standard band, respectively [26,28]. In this article, solvent CHCl_3 were utilized as an internal standard. The 918 cm^{-1} absolute Raman cross section σ_S of the CH_3CN at 488 nm laser excitation was determined to be $1 \times 10^{-30}\text{ cm}^2\text{ molecule}^{-1}$ [28–30].

3. Results and discussion

Full geometry optimization was performed to find the most stable structure as the initial point for further calculations for both the ET monomer and the dimers structure. Fig. 1 shows the B3LYP/6-311G (d,p) computed geometries of ET and its dimers. No

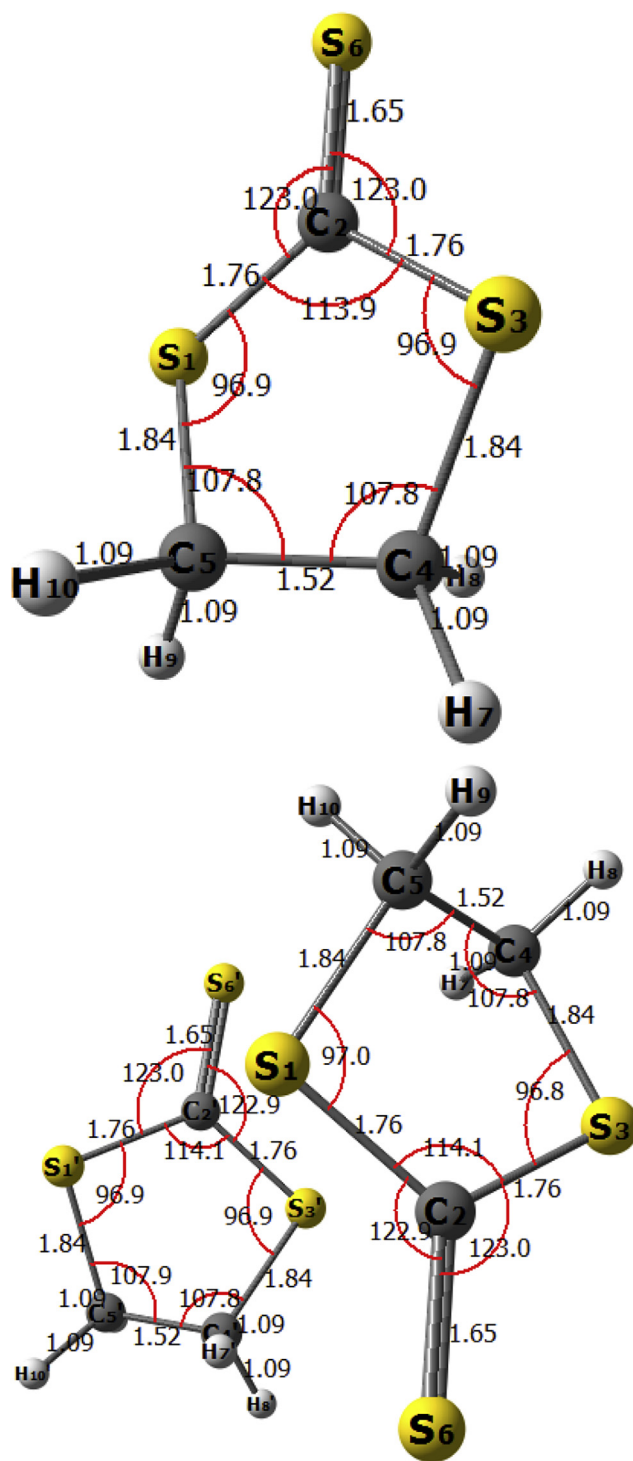


Fig. 1. B3LYP/6-311G (d,p) computed geometry parameters of ET and its dimers with bond lengths (in angstroms) and bond angles (in degrees) indicated.

imaginary vibrational frequencies were found in the further calculation.

Selected optimized parameters of the ET monomers and dimers in gas phase are presented in Table 1 for minimum energy geometry. The visual inspection with the use of GAUSSVIEW 3.0 helps us to estimate the dihedral angles (which are also included in Table 1). Table 1 shows that, no significant bond length and bond angles differences exist between the ET monomers and dimers.

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