Journal of Molecular Liquids xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Raman spectroscopic study of polar aprotic molecule and its molecular associations with chemical and isotopic solvents: Comparative study with quantum-chemical calculations

Ganesh Upadhyay, Th. Gomti Devi *

Department of Physics, North-Eastern Regional Institute of Science and Technology, Arunachal Pradesh 791109, India

ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form 8 May 2014
Accepted 21 May 2014
Available online xxxx

Keywords:
Bandwidth
Peak frequency
Isotropic
Vibrational relaxation
Dimer

ABSTRACT

Raman spectroscopic technique was used to study the intermolecular interactions and dynamics of S═O stretching vibration of dimethyl sulfoxide (DMSO) molecule using different chemical and isotopic solvents. The Raman bands have been deconvoluted into four distinct bands for neat DMSO and in binary mixtures. Deconvoluted bands in neat DMSO were assigned as monomer, cyclic out-of-phase, cyclic in-phase and chain dimers having peak frequencies 1069.10, 1056.60, 1041.50 and 1027.30 cm^{-1} respectively. The vibrational relaxation phenomena of the systems have been studied. Quantum-chemical calculations have been carried out to gain more insight into the self-association of DMSO and its interacting environment with the solvents using the HF/6–31 + G (d, p) method. Theoretical calculations have been compared with the experimental results and we obtained in good agreement of the results.

1. Introduction

Raman spectroscopy has been recognized as the powerful tool for determining important features and structure dynamics of liquid molecules. Most of the features have been studied based on the bandshape of the recorded Raman spectra. The nature of a Raman band provides certain properties such as the type of vibration, scattering geometry, optical property of the detecting system, polarization of bond and dipole, dispersion and repulsive interactions [1–7]. Generally, Raman bands are characterized by some band parameters such as peak position, bandwidth, band area and intensity respectively. However, the pieces of information acquired from the raw spectra using such parameters are somewhat uncertain in some occasions as the Raman bands tend to broaden due to the overlapping of weak combination or overtone bands and self-association of molecules.

Deconvolution of a broad band using a curve fitting technique is considered as the best way to analyze the broad band. Various researchers have been working on different molecules using a deconvolution technique [1,8–12]. It is necessary to determine the number of bands to be included for deconvoluting a given envelope of a broad band. The deconvolution technique provides well resolved spectra by narrowing the spectral components.

Vibrational relaxation study of liquid molecules in binary mixture system provides valuable information about the dynamics of the molecules. In our study vibrational relaxation of DMSO has been carried out using isotropic Raman component which provides the direct information about the dephasing phenomena [13]. Various researchers studied vibrational relaxation using isotropic Raman components [7–10,13–15]. In the paper [13], researchers studied vibrational relaxation of liquid phenylacetylene in methylcyclohexane solvent using Raman and IR bandshape analysis. They tested experimental results with various models on vibrational relaxation processes. Kolodzieski et al. [14] carried out vibrational dephasing phenomena in bromocyclohexane using methylcyclohexane, methanol, 1-propanol and 2-propanol solvents. The study provides a framework for elucidating the differences in vibrational dynamics of various conformers. Abramcyzyk and Moszkowska [15] studied the vibrational dynamics and static properties of the CH_2 rocking mode of methylcyclohexane as a function of temperature and cooling rate using polarized Raman components. As per their studies, vibrational dynamics as well as static properties are very sensitive indicators to specify phases and phase transition at the molecular level.

Nowadays, simulation methods such as Monte Carlo (MC) and molecular dynamic (MD) simulations have been used to study the vibrational relaxation [6,16–20]. Such simulation study helps in interpreting the experimental results obtained from the polarized Raman spectroscopy. Musso et al. [6] studied the change in band profile parameters due to concentration fluctuations in C═O stretching mode of acetone in CCl_4 solvent. Experimental results were well supported

* Corresponding author. Tel.: +91 360 2257401x6144; fax: +91 360 2244307.
E-mail addresses: ganeshupadhyay43@yahoo.in (G. Upadhyay), devigomti@yahoo.co.in (T.G. Devi).

http://dx.doi.org/10.1016/j.molliq.2014.05.014
0167-7322/

with the results of MC simulations. Singh et al. [20] carried out a detailed analysis on polarized Raman spectral change of hydrogen-bonded 2- and 3-chloropyridine with methanol. They performed theoretical DFT calculations and compared the experimental data using polarized Raman spectroscopy. They obtained an excellent match of the experimental and theoretical spectra with the B3LYP/6–31 + G (d, p) method.

A brief review of the studies done on DMSO by various researchers has been stated in our previous paper [2]. To the best of our knowledge, limited study has been done for DMSO at different deuterated solvents. In the paper [2], we have studied elaborately the noncoincidence effect (NCE) of S═O stretching mode of DMSO molecule at different chemical and deuterated solvents. We obtained interesting information about the interacting system and theoretical models were in good agreement with our experimental data. As the bandshape of S═O stretching vibration of DMSO is a broad band, there may be chances of formation of self associations among the molecules. In order to study about the different associations of molecules involved in this molecule and at different binary mixtures, we deconvoluted the band into four distinct components and assigned them in different association states such as monomer, cyclic dimer out-of-phase, cyclic dimer in-phase and chain dimer [8]. To have a clear picture about the interacting nature within solute

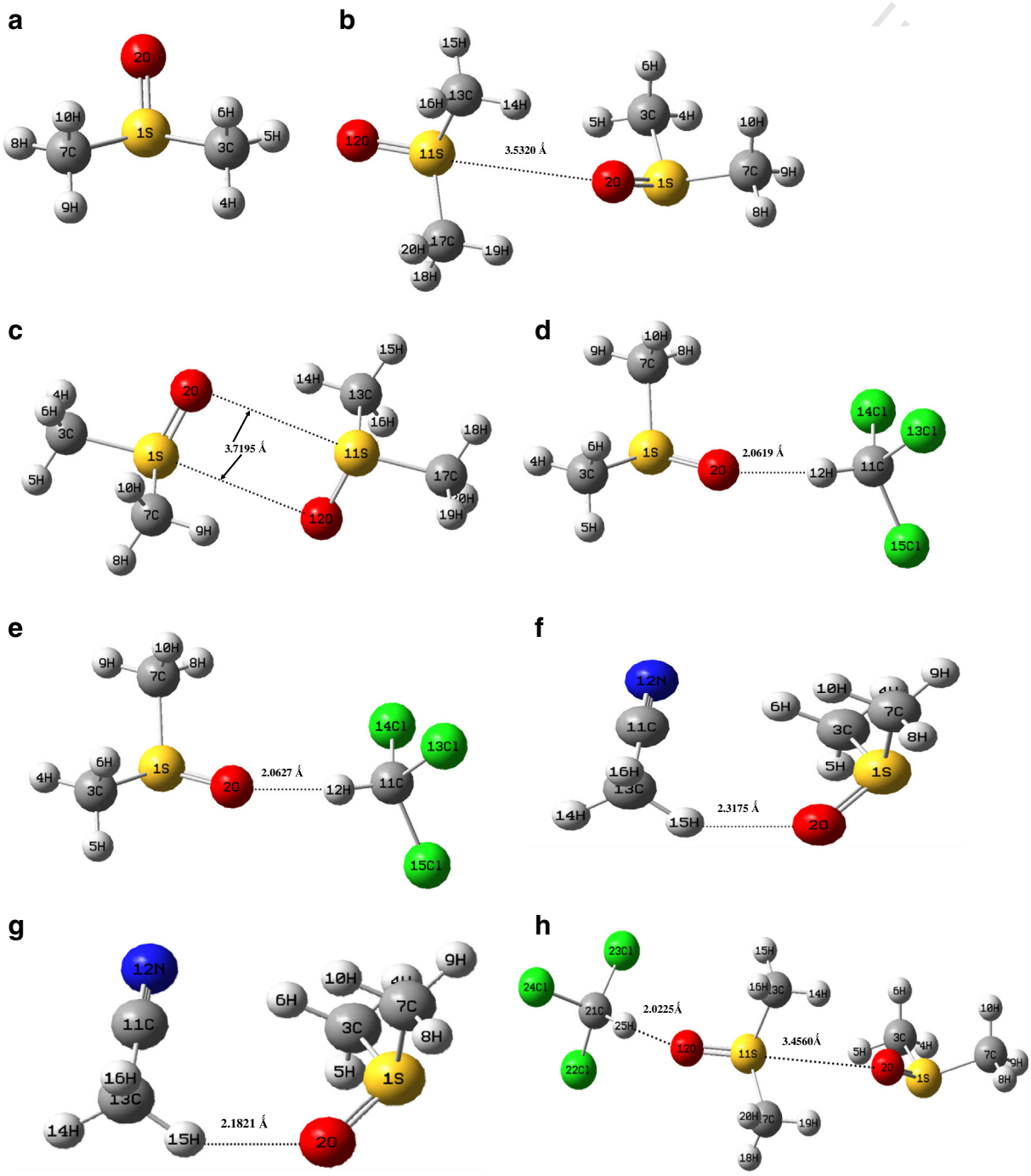

Fig. 1. Optimized structures of monomer, chain dimer and cyclic dimers of DMSO and their interactions with CLF, CLFd, ACN and ACNd solvents- (a) DMSO monomer, (b) chain dimer of DMSO, (c) cyclic dimer of DMSO, (d) DMSO + CLF, (e) DMSO + CLFd, (f) DMSO + ACN, (g) DMSO + ACNd, (h) chain dimer of DMSO + CLF, (i) chain dimer of DMSO + CLFd, (j) chain dimer of DMSO + ACN, (k) chain dimer of DMSO + ACNd, (l) cyclic dimer of DMSO + CLF, (m) cyclic dimer of DMSO + CLFd, (n) cyclic dimer of DMSO + ACN and (o) cyclic dimer of DMSO + ACNd.

Please cite this article as: G. Upadhyay, T.G. Devi, Raman spectroscopic study of polar aprotic molecule and its molecular associations with chemical and isotopic solvents: Comparativ..., Journal of Molecular Liquids (2014), http://dx.doi.org/10.1016/j.molliq.2014.05.014