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# Photoabsorption and photodissociation studies of dimethyl sulphoxide (DMSO) in the 35,000–80,000 cm$^{-1}$ region using synchrotron radiation

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ABSTRACT

Photoabsorption and photodissociation studies of dimethyl sulphoxide and its deuterated isotopologue (DMSO-$h_6$ and DMSO-$d_6$) are performed using synchrotron radiation in the 35,000–80,000 cm$^{-1}$ region. In the photoabsorption spectrum, Rydberg series converging to the first three ionization potentials of DMSO at 9.1, 10.1 and 12.3 eV corresponding to removal of an electron from the highest three occupied molecular orbitals (14a′, 7a″ and 13a′) are observed. Based on a quantum defect analysis, Rydberg series assignments are extended to higher members as compared to earlier works and a few ambiguities in earlier assignments are clarified. Analysis is aided by quantum chemical calculations using the DFT and TDDFT methodologies. Vibronic structures observed in the spectrum of DMSO-$h_6$ in the regions 7.7–8.1 eV and 8.1–8.8 eV are attributed to the transitions 7a″ → 4p at 7.862 eV and 14a′ → 6s/4d at 8.182 eV, respectively. Photoabsorption spectra of DMSO-$h_6$ and -$d_6$ recorded using a broad band incident radiation show prominent peaks, which are identified and assigned to electronic and vibronic transitions of the SO radical. This provides a direct confirmation of the fact that DMSO preferentially dissociates into $CH_3$ and SO upon UV–VUV excitation, as proposed in earlier photodissociation studies. An extended vibronic band system associated with the $e^1\Pi$–$X^3\Sigma^-$ transition of the SO radical is identified and assigned. The complete VUV photoabsorption spectrum of DMSO-$d_6$ is also reported here for the first time.

## 1. Introduction

Dimethyl sulphoxide (DMSO) is the simplest member of the sulphoxide family of compounds. It is a versatile solvent widely used in industrial applications and is a natural product of biodegradation of organo-sulphur compounds in the biosphere [1]. It is postulated to be an intermediate in the atmospheric oxidation of alkyl sulphides to sulphur dioxide [2]. The electronic structure of DMSO and its photodissociation dynamics have elicited considerable interest due to its important role in the atmospheric sulphur balance [3]. Understanding the excited states of DMSO is of crucial importance in understanding photochemical reactions involving this compound.

The electronically excited states of DMSO have been studied by a variety of experimental and theoretical methods [1,3–7]. The earliest study of the electronic

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absorption spectrum of DMSO was by Gollnick and Stracke [4]. Subsequently, Sze et al. [5] reported photoabsorption and electron energy loss studies together with some theoretical calculations. Recently, the photoabsorption spectrum of DMSO in the region 30,000–87,000 $cm^{-1}$ using synchrotron radiation (SR) has been reported by Drage et al. [1]. However, Rydberg series and vibronic analysis of the observed transitions reported in literature [1,5] is incomplete and assignments by different authors are often at variance. The motivation behind the present work is to sort out some of these issues and obtain a complete set of Rydberg series and vibronic assignments for the electronic absorption spectrum of DMSO. Isotopic substitution is a valuable tool for confirmation of vibrational assignments as seen from some of our earlier works [8,9]. In this context, it is of interest to examine the VUV photoabsorption spectrum of the deuterated isotopologue DSMO-$d_6$, on which we do not find any VUV photoabsorption study reported earlier. In the present work, photoabsorption spectra of DMSO-$h_6$ and DMSO-$d_6$ are studied in the region 35,000–80,000 $cm^{-1}$ ($\sim$4.3–9.9 eV) using SR. Details of the experiments performed and the analysis of the spectra carried out with the help of quantum chemical calculations are presented in this paper. Some interesting observations pertaining to the photodissociation of DMSO upon VUV excitation are also discussed.

## 2. Experimental

Experiments are performed at Indus-1 SR source at the Raja Ramanna Centre for Advanced Technology, Indore, India. Photoabsorption spectra are recorded using two VUV beamlines at Indus-1, i.e., the Photophysics [10] and High Resolution Vacuum Ultra-Violet (HRVUV) beamlines [11]. The Photophysics beamline is a medium resolution beamline built around a 1 m Seya-Namioka monochromator and delivers a monochromatic beam at the sample position. The average spectral resolution is 1.5 Å, which corresponds to $\sim$4 meV at 4 eV and $\sim$9 meV at 9 eV. A 25 cm SS absorption cell isolated from the beamline by an LiF window (transmission cut-off $\sim$95,240 $cm^{-1}$) mounted on a gate valve is used for the gas phase studies. Atomic lines of xenon are used for wavelength calibration. The HRVUV beamline is based on a 6.65 m off-plane Eagle spectrometer and offers higher resolution (average resolution 0.3 Å, which corresponds to $\sim$1.3 meV at 4 eV and $\sim$3 meV at 9 eV). In this configuration, the broad band SR passes through a 3 mirror optical system and through the gas cell after which it is focused onto the entrance slit of the spectrometer. A 50 cm SS absorption cell, which is isolated from the spectrometer and fore-optics by two $CaF_2$ (transmission cut-off $\sim$80,000 $cm^{-1}$) windowed gate valves on either end, is used for photoabsorption studies. For a central wavelength ($\lambda_0$) set by the grating, the spectrum is recorded in a 200 Å region ($\lambda_0 \pm 100$ Å) by scanning PMT cum exit slit on the Rowland circle. Details of the beamline and also the wavelength scanning mechanism are reported in our earlier publication [11]. Wavelength calibration is done using xenon atomic absorption lines (in the region $>$62,500 $cm^{-1}$) or absorption bands of molecules like $O_2$ and $SO_2$ (in the region 48,000–62,500 $cm^{-1}$).

DMSO-$h_6$ and DMSO-$d_6$ of stated purities 99% supplied by M/s. Sigma Aldrich and Heavy Water Board, Baroda, India, respectively, are used. Samples are subjected to several freeze–pump–thaw cycles before introduction into the cells. The absorption cells are evacuated to a base pressure of $\sim 10^{-6}$ mbar prior to sample introduction. Absorption spectra are generated using the well-known Beer–Lambert law: $A = \ln(I_0/I)$, where $A$ is the absorbance, $I_0$ and $I$ are the transmitted intensities with and without sample, respectively. Capacitance gauges are used to measure the sample pressure, which is varied from $\sim$0.001 to 1 mbar in order to take care of the varying absorption cross sections in the vast wavelength region covered. In both the beamlines, the dispersed light is detected using a sodium salicylate-coated visible PMT and the absorption signal is normalized with respect to the synchrotron beam current.

## 3. Computational

DMSO belongs to the $C_s$ point group, with the mirror plane passing through the S=O bond. Its ground state configuration is given by [*core*] $(7a')^2(8a')^2(3a'')^2(9a')^2(10a')^2(11a')^2(4a'')^2(5a'')^2(12a')^2(6a'')^2(13a')^2(7a'')^2(14a')^2$: $X^1A'$. DMSO is the sulphur analogue of the well-studied acetone molecule [2]. The simple molecular orbital (MO) picture in the acetone molecule where the highest occupied MO (HOMO) is a lone pair localized on the oxygen atom is disturbed in DMSO, as the sulphur d orbitals also contribute to the MOs and considerable delocalization is seen [4]. Contour plots of the three HOMOs and three lowest unoccupied MOs (LUMOs) obtained in the present computation are visualized using the MacMolPlt software [12] as shown in Table 1.

Results of ground state geometry optimization for the neutral and ionized molecule, carried out using the density functional theory (DFT) as well as the Møller–Plesset second order perturbation theory (MP2) methods are listed in Tables 2 and 3. Correlation functionals used for DFT calculations are Becke-3–Lee–Yang–Par (B3LYP) [13,14], CAM-B3LYP [15] and Perdrew–Burke–Ernzerhof (PPBE0) [16]. The theoretical and experimental values of bond lengths and bond angles [17,18] of DMSO are in good agreement, while for $DMSO^+$, experimental data is not available in literature. It may be seen from Tables 2 and 3 that ionization of the molecule does not result in much change in the S–O and S–C bond lengths, but there is considerable change in the bond angles O–S–C and C–S–C. This suggests a preference for excitation of bending modes rather than stretching modes upon ionization and/or excitation to Rydberg states. Ground state vibrational frequencies for both neutral and ionized species at the B3LYP/cc-pV5Z level of theory are listed in Table 4. Ionic frequencies are calculated in the anticipation of their use in the assignment of vibronic bands associated with Rydberg transitions [19]. Since there are no experimental or theoretical values of vibrational frequencies available for $DMSO^+$, these are calculated and reported here for the first time (cf. Table 4).

The first few vertical excited singlet states of DMSO have been reported recently using time dependent DFT (TDDFT) [3,21], multireference configuration interaction