Synchrotron based VUV spectroscopy in gas and matrix isolated phase

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Using indigenously developed beamlines and experimental work stations at Indus-1 (450MeV) synchrotron radiation source, VUV photoabsorption spectroscopy of polyatomic molecules in gas and matrix isolated phases is performed. Issues pertaining to electronic structure, vibrational modes, vibronic interactions, geometries and symmetries of excited states of molecules are clarified using gas phase studies [1]. On the other hand, the matrix isolation spectroscopy technique under cryogenic temperatures in conjunction with a synchrotron source is used to develop understanding of valence or Rydberg character of excited states of isolated molecules in rare gas matrices and molecular processes in astrophysical ices [2]. *ab initio* quantum chemical calculations are used for interpretations of the observed spectra.

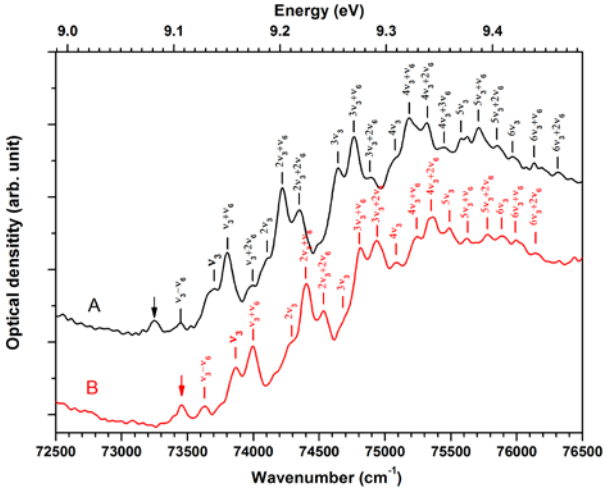

Fig. 1: $1a_2 \rightarrow 4p$ system of $CHCl_3$ (curve A) and $CDCl_3$ (curve B). For clarity of presentation, curve A is displaced vertically from curve B.

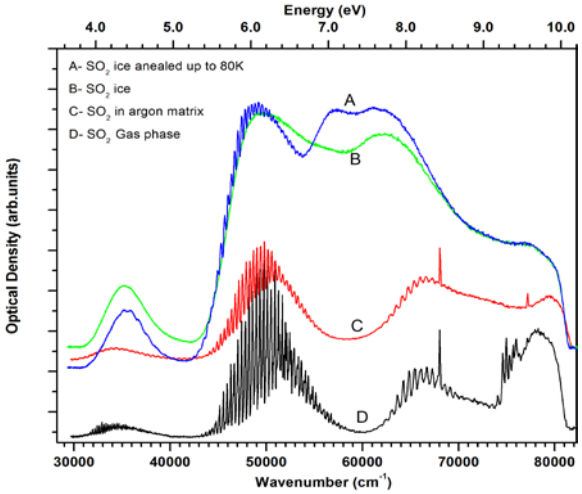

Fig. 2: VUV absorption spectrum of SO_2 in gas phase, isolated in argon matrix and ice phase. Curve D is displayed vertically down from others for clarity.

From analysis of SO_2 spectra, we observed that dominating excitations giving rise to $\tilde{E} - \tilde{X}$ system are $\tilde{X}\ ^1A_1 \rightarrow 3^1A_1$, 2^1A_1 and 2^1B_1 and the vibrational features are mainly due to excitation of the modes ($\nu_1 + \nu_2$) and ($\nu_2 + \nu_3$) with some contributions from ν_1 and ν_3. In case of chloroform (Fig.1), vibrational progressions observed in the region of 72,500 – 76,500 cm^{-1} are reassigned to ν_3 and ($\nu_3 + \nu_6$) belonging to the $1a_2 \rightarrow 4p$ transition in contrast to earlier assignment of ν_3 progression of the $3e \rightarrow 4p$ Rydberg transition. Quantum defect values are found to be consistent with excitation from the chlorine lone pair orbitals. Matrix isolated spectra of SO_2 (Fig.2) in Argon show blue shift for most of observed band systems. Detailed investigations of VUV spectra of the chloroform, SO_2, and acetone will be presented.

[1] Param Jeet Singh *et. al.* J Quant. Spectrosc. Radiat. Transf. - (a). In Press, Corrected Proof (2013) (b). **114,** 20 (2013); (c). **113**, 1553 (2012); (d) **113**, 267 (2012).
[2] N.J. Mason et.al. Faraday Discuss., 133, 311(2006).