

IR-VUV studies of 3-buten-2-ol monomer and multimers in a molecular beam.

(Tokyo Institute of Technology) OJonathan R. Woodward, Hirokazu Watanabe.
Mitsuhiko Miyazaki, Shun-ichi Ishiuchi and Masaaki Fujii

[Introduction] Direct vacuum-ultraviolet (VUV) photoionization of molecules in molecular beams with mass-spectrometric detection is a powerful complementary technique to multiphoton ionization techniques like REMPI (Resonance Enhanced Multi-Photon Ionization). It allows mass-selective spectroscopic measurements of molecules with inaccessible excited states or those possessing states with extremely short lifetimes. By combining pulsed VUV photoexcitation with pre- or post- IR excitation it is possible to record the infrared spectra of both ground state jet-cooled molecules¹ and ion-like Rydberg states² with high spectral resolution and sensitivity. Here we discuss the development of our instrumentation, its application to some example model systems and its use in examining the conformational structure of 3-buten-2-ol in a molecular beam and the structure and reactivity of its multimers.

[Instrumentation] VUV generation is achieved via a 4-wave mixing scheme in Kr or Xe gas. Figure 1 shows the experimental layout of the spectrometer.

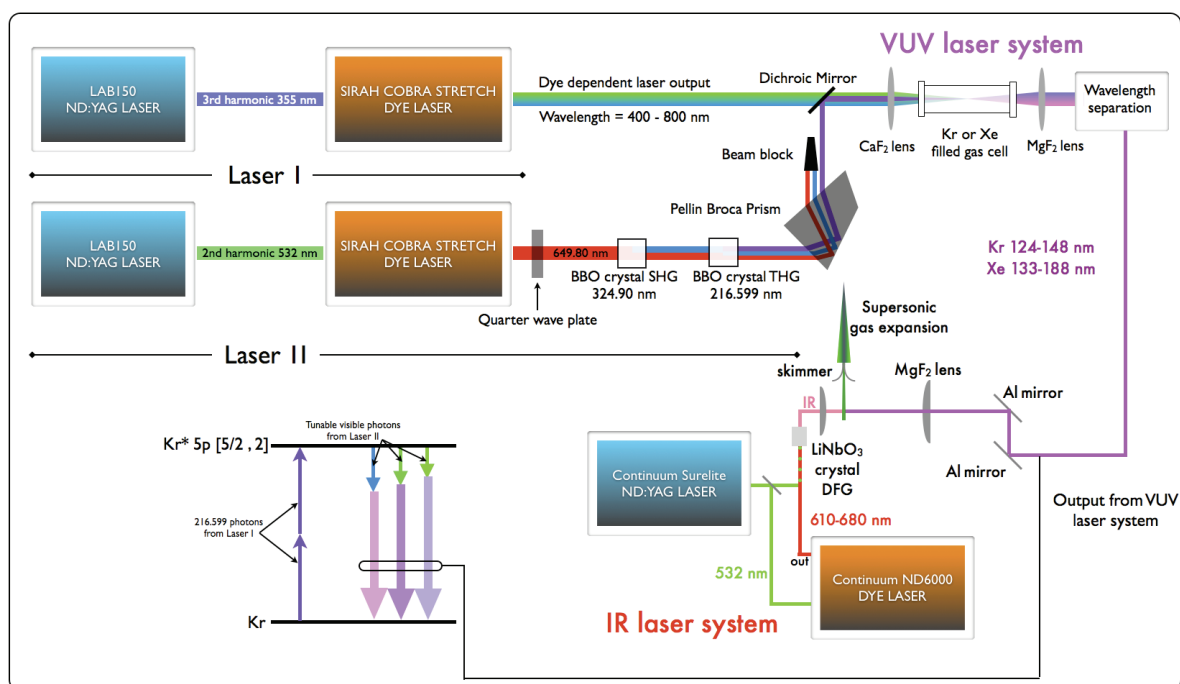


Figure 1. Experimental arrangement for the measurement of IR-VUV spectra of molecules in a supersonic jet expansion.

The VUV output of the laser, tuneable to an extent defined by the dye employed in laser I, is focussed onto the molecular beam, and is free of any of the other wavelengths employed in its generation. In this work, all VUV generation was performed with Kr gas, with phase matching achieved by tuning of the gas pressure. In order to record photoionization threshold spectra free from any Kr re-absorption

features, small amounts of a low ionization potential calibrant molecule (triethylamine in this work) is also seeded in the molecular beam. In addition, this provides VUV power calibration across the tuning region. The IR laser can access the spectral region from approximately 2800 – 3800 cm^{-1} ; a useful region for the examination of C-H, O-H and N-H stretching vibrations. IR-VUV spectra of molecular ground states are recorded by adjusting the VUV wavelength to below the ionization threshold and sweeping the IR frequency, which is applied 50 ns before the VUV excitation.

[Experimental] 3-buten-2-ol is an ideal molecule for use in the study of stereoelectronic effects due to the potential interaction between its neighbouring alkene and alcohol moieties³. Previous studies have remained somewhat inconclusive in determining which conformers are present in 3-buten-2-ol vapour at room temperature. We have used VUV and IR-VUV photoionization methods to examine this molecule and its ability to form multimers in a molecular beam. Figure 2 shows the mass spectrum obtained by VUV irradiation of 3-buten-2-ol at 129 nm. The 3-buten-2-ol ion is clearly observed (and is free of fragmentation) along with an extended series of multimer peaks.

Of particular note is the surprisingly broad signals observed for the dimer and higher multimers. This is suggestive of their decomposition within the mass spectrometer. Intriguingly, mass spectral signals are observed which correspond to masses of 15 and 18 mass units less than the dimer signal (mass = 144), which appear to correspond to the loss of methyl and water respectively.

Similar peaks appear corresponding to the trimer, but the tetramer shows only a peak corresponding to a loss of mass 15. Monomer and dimers show weak peaks corresponding to water cluster formation. The water clusters become more prominent for larger multimers and for the octomer, the water cluster signal is larger than the octomer itself. The inset shows the photoionization threshold spectrum of the monomer. We have recorded the IR-VUV spectrum of the monomer in the C-H and O-H regions and discuss the observed spectra in comparison with the results of DFT calculations. The threshold and IR-VUV spectra of the dimer are proving more difficult to successfully record. This difficulty may lie in the decomposition process of the multimers, including dissociation from the larger clusters. Experiments are underway to overcome these difficulties.

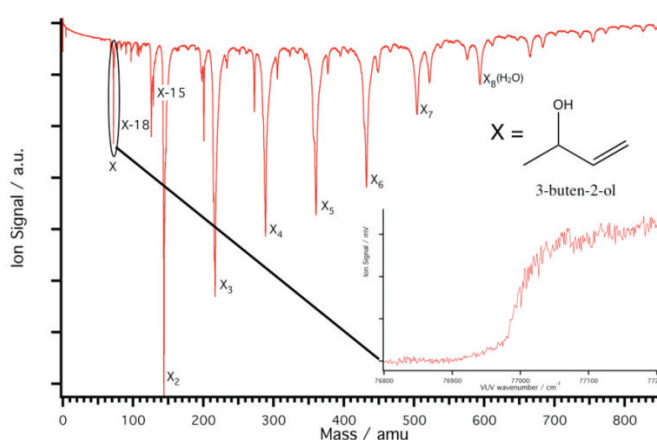


Figure 2. Mass spectrum obtained from the 129 nm irradiation of 3-buten-2-ol. The inset shows the ionization threshold spectrum of 3-buten-2-ol.

1. H. K. Woo, P. Wang, K.-C. Lau, X. Xing, C. Chang and C. Y. Ng; *J. Chem. Phys.* **119** (8), 2003, 9333.
2. A. Fujii, A. Iwasaki, T. Ebata, N. Mikami, *J. Phys. Chem. A.* **101**, 1997, 5963.
3. I. F. Shishkov, S. Shlykov, B. Rousseau, Z. H. Peng, C. Van Alsenoy, H. J. Geise, O. N. Kataeva, W. A. Herrebout and B. Van der Veken., *J. Phys. Chem. A*, **105**, 2001, 1039.