

イソプレンを含む分子錯体のマトリックス単離分光 (産総研) ○伊藤文之

Matrix-isolation IR spectroscopy of isoprene and its hydrate complex
(AIST) ○Fumiyuki Ito

1. Introduction

Isoprene (2-methyl-1,3-butadiene) is one of the most abundant volatile organic compounds (VOCs) in the troposphere with a global emission of ~500 Tg per year ¹⁾. It reacts with OH radicals, ozone, and NO_x to produce low-volatility compounds, which are finally converted to secondary organic aerosols (SOAs) via subsequent complex physico-chemical processes, influencing the climate and urban air quality ²⁾. In-situ detection of this molecule using spectroscopic technique is thus of fundamental importance in the field of atmospheric chemistry. The assignments of fundamental bands of this molecule have not settled yet, however, due to the lack of well-resolved vibrational spectra.

The present paper reports the first observation of matrix-isolation IR spectrum of isoprene in noble gas matrices, and the assignments of the fundamental bands in combination with quantum chemical calculations ³⁾. We will also report on the isoprene-H₂O complex which has atmospheric relevance ⁴⁾.

2. Experimental

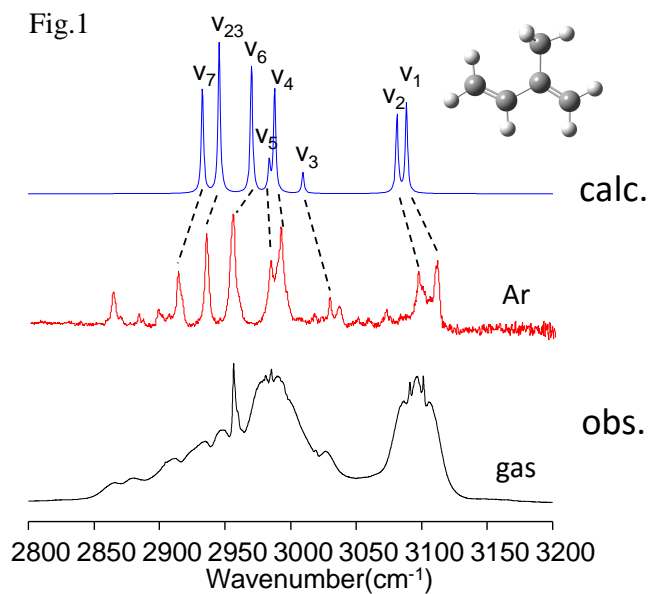
Isoprene was purchased from Wako Pure Chemical Industry (Osaka, Japan), and used after degassing via freeze-pump-thaw cycles. Premixed samples of isoprene and H₂O were prepared by mixing the vapors and noble gas (Ar or Kr) at various ratios in a stainless steel vessel. Each gaseous sample was deposited onto a cold CsI surface maintained at 20 K for Ar and 25 K for Kr matrices. FTIR spectra of matrix-isolated isoprene and its water complexes were measured by JASCO FTIR-6100 spectrometer with a resolution of 0.5 cm⁻¹.

3. Calculations

All calculations were done with the Gaussian09 (Rev. A.02.) package. For isoprene, calculations were done at the B3LYP/6-311++G(3df,3pd) level. For the isoprene-H₂O complex, on the other hand, DCP-B3LYP/6-31+G(2d,2p) and MP2/6-31+G(2d,2p) levels of theory were employed for structure optimization and vibrational calculations, in order to incorporate dispersion interaction. In view of the results of the calculations for seven possible initial guesses, we concluded that the OH--π complex is the global minimum of the potential energy surface for the isoprene-H₂O system. The binding energy of the isoprene-H₂O complex, calculated to be 1364 cm⁻¹, is comparable to that of benzene-H₂O complex. ⁵⁾

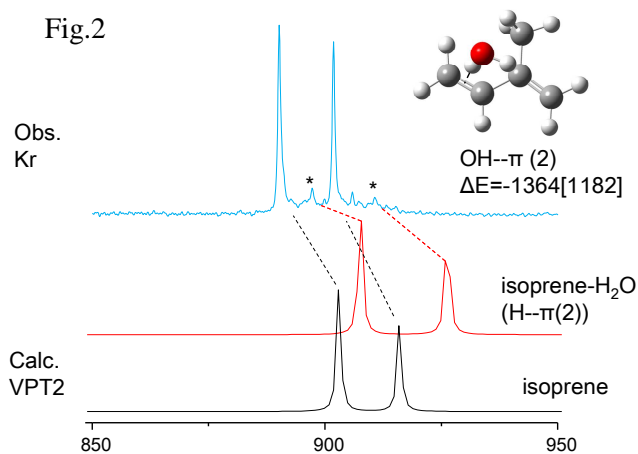
4. Results and Discussions

Fig. 1 shows the matrix-isolation spectrum of isoprene in Ar matrix in comparison with predicted vibrational peaks from anharmonic (VPT2) DFT calculation. The congested spectrum in the C-H stretching region was well-resolved at cryogenic temperature (20 K) and a good agreement was found with the theoretical simulation. We presented the alternative vibrational assignments for the weak bands in the out-of-plane bending region, from a careful comparison with the recent gas-phase study. ⁶⁾



In Fig. 2 the spectrum of the isoprene- H_2O complex in Kr matrix is compared with the VPT2 calculation. The calculation well reproduces the positions of small satellites in the skeletal out-of-plane bending region. A reasonable agreement was found in other vibrational modes.

The present study suggests that the change in the charge distribution of isoprene due to the formation of a complex with H_2O may lead to alteration of the reactivity with respect to the insertion of OH radicals, thereby influencing the formation of aerosols in the atmosphere.



References

- 1) Guenther *et al.*, *Atmos. Chem. Phys.* **6**, 3181 (2006).
- 2) Surratt *et al.*, *PNAS* **107**, 6640 (2010).
- 3) F. Ito, *JMS*, in press.
- 4) F. Ito, *JMS* **341**, 27 (2017).
- 5) J. Rezac *et al.* *J. Chem. Theory Comput.* **7** (2011) 3466.
- 6) Brauer *et al.*, *Atmos. Meas. Tech.* **7** (2014) 3839.