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中赤外分光による尿酸 - 水及びメラミン錯体の水素結合構造解析

（横浜市立大院・生命ナノ）○三枝　洋之, 中村 大介, 浦島　周平

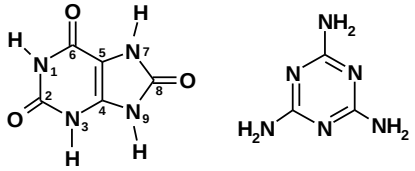
Hydrogen-bonding interactions of uric acid complexes with water/melamine revealed by mid-infrared spectroscopy

(Graduate School for Bio- and Nanosystem Sciences, Yokohama City Univ.) ○H. Saigusa, D. Nakamura and S. Urashima

1. INTRODUCTION

The structures of most biomolecules are determined by the corrective influence of many weak interactions. Among them, H-bonding interactions of biomolecules with water are particularly important in the stabilization of specific conformations that can exhibit biological functions. Therefore, identification of both donor (D) and acceptor (A) sites involved in H-bonding is essential for molecular understanding of the relation between the structural features and proper functioning.

Chart 1. Structures of uric acid (UA) and melamine (MEL).



In the present work, H-bonding interactions of uric acid (UA, Chart 1) complexes with water/melamine (MEL) have been investigated via IR–UV double resonance measurements in the mid-IR region, to elucidate how hydration/complexation to a specific CO site of UA affects the frequency and intensity of this stretching mode and others. It is found that hydration to the C8O position of UA (Chart 1) enables for coupling of this stretch mode with C2O mode. By using this mid-IR signature of H-bonding, the 1:1 complex of UA and MEL (UA−MEL) we reported previously is unequivocally identified as the calculated most stable structure, in agreement with our assignment made based on the near-IR measurement[1,2].

2. EXPERIMENTAL

Hydrated cluster of UA and 1:1 complex of UA−MEL formed by the laser-desorption/supersonic-jet method were ionized through resonant two-photon ionization (R2PI) using a frequency tunable UV laser, and analyzed by a TOF mass spectrometer. Mass-selected UV spectra were recorded by probing ion signal at a particular mass channel while scanning UV laser frequency. IR spectra were recorded in the mid-IR (1500−1800 cm^{-1}) by the conventional IR−UV double-resonance scheme.

3. RESULTS AND DISCUSSION

In our previous work, two structurally different monohydrates of UA were found and assigned to the two most stable isomers, both with UA in its triketo

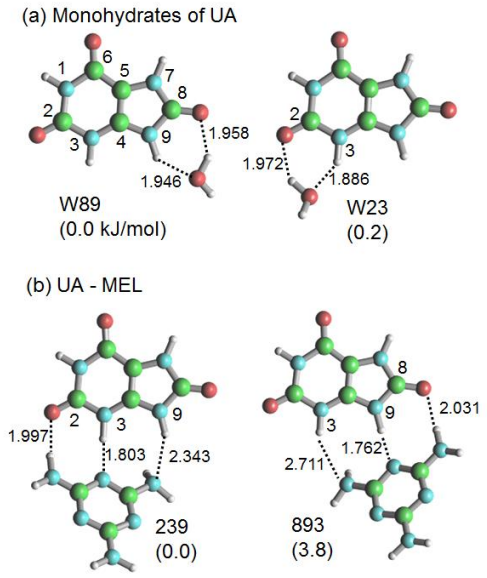


Fig. 1. The two lowest-energy structures calculated for (a) UA monohydrate and (b) UA−MEL complex. Relative stabilization energies are shown in kJ/mol. Formation of H-bond is indicated by the dotted line with its distance in Å.

form and denoted W23 and W89 as shown in Fig. 1(a). The mid-IR spectra recorded for the two monohydrates, together with that of monomer, are shown in Fig. 2. The monomer spectrum in Fig. 2(a) shows three strong bands at 1744, 1765, and 1798 cm^{-1}, which are assignable to C6O, C2O, and C8O stretching vibrations, respectively, in comparison with the calculated spectra. The potential energy distribution analysis provided by DFT frequency calculation [3] indicates that C2O and C8O 'internal' modes of UA are somewhat coupled each other, and thus the bands at 1765 and 1798 cm^{-1} are ascribed more precisely to their out-of-phase [C2O(65%)–C8O(14%)] and in-phase [C8O(62%)+C2O(12%)] contributions, respectively.

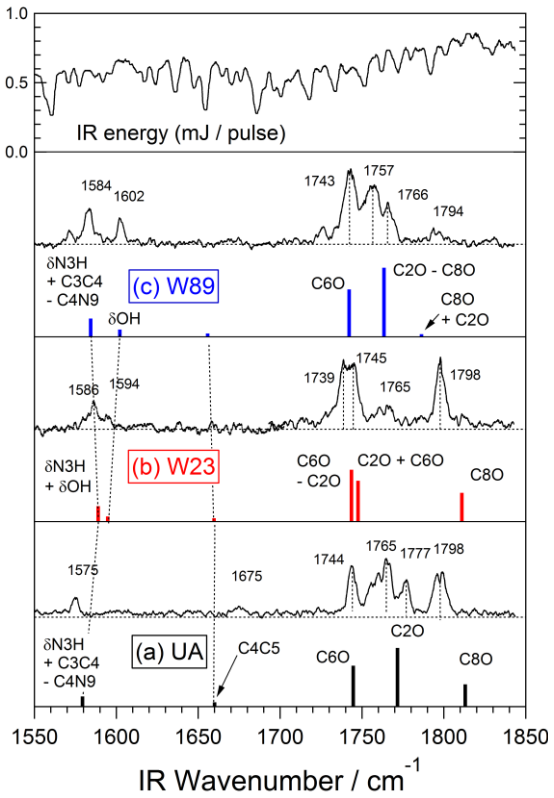


Fig. 2. Mid-IR spectra recorded for (a) UA monomer, and two monohydrates (b) W23 and (c) W89. Vibrational spectra calculated at the B3LYP/6-311++G(d,p) level (scaled by a factor of 0.982) are also shown. Energy curve of the mid-IR laser is shown in top panel.

The mid-IR spectrum obtained for the monohydrate W23 [Fig. 2(b)] shows a prominent band at 1798 cm^{-1}, which is predominantly due to C8O mode. This mode decoupling is explained to occur as a result of H-bonding to the C2O site. The reduction of its stretching frequency, in turn, allows for coupling with C6O stretch mode. Therefore, the doublet structure observed at 1745 and 1739 cm^{-1} can be associated with the in-phase and out-of-phase contributions of the two stretch modes C2O ± C6O.

The normal mode analysis for isomer W89 indicates that H-bonding at the C8O site mediates vibrational coupling of this mode with C2O mode. Accordingly, the calculated two transitions in Fig. 2(c) are better described by the in-phase and out-of-phase combinations of the two internal modes with nearly equal contributions. In this case, the C8O and C2O stretch motions are almost in the opposite directions, and thus the IR activity of their symmetric combination (C8O + C2O) is substantially suppressed as manifested in Fig. 2(c). This also suggests that the strong band at 1757 cm^{-1} can be assigned to the out-of-phase (antisymmetric) combination of the two stretch modes (C2O – C8O).

Our previous result of the UA−MEL complex obtained in the near-IR region suggested that the observed 1:1 complex is either structure 239 or 893 shown in Fig. 1(b). Here, we demonstrate that the mid-IR signature of H-bonding derived from the result of the monohydrate is essential to assign the structure of the UA−MEL complex. Details of the mid-IR spectra and application of 'mid-IR labelled UV spectroscopy' to isomer identification will be discussed.

REFERENCES

[1] H. Asami et al., The 8th Annual Meeting for Molecular Science (2014, Hiroshima, 2A06). [2] H. Asami and H. Saigusa, *J. Phys. Chem. B*, **118**, 4851 (2014). [3] M. Majoube and G. Vergoten, *J. Mol. Struct.*, **294**, 41 (1993).