1B04

水ダイマーの振動前期解離に対する理論研究

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Infrared(IR)-induced predissociation of water is considered to be an important reaction dynamics of water, but due to the complicated structure of the water cluster, direct measurement of the IR induced predissociation rate constant is difficult. Therefore, the water dimer is expected to play an important role as a smallest water cluster to measure the predissociation rate. However, the vibrational predissociation mechanism of hydrogen bonding water cluster is less understood at present stage.

In our work infrared-induced vibrational predissociation (VPD) of water dimer (See Fig. 1) were developed in the adiabatic model and applied to the calculation of the VPD rate constant from a single vibrational level of high-frequency vibrational mode. The vibrational modes of the donor and accepter H_2O units of water dimer were grouped to high-frequency degrees of freedom and the intermolecular modes were grouped to the low frequency-degrees of freedom in the adiabatic description (Table 1).

The VPD process of water dimer can be classified into two mechanisms: one is the direct mechanism in which the vibrational energy of the high-frequency mode excited directly flows into the final fragment state; the second one is called the sequential mechanism in which the high-frequency vibrational energy is transferred to the final state via resonant intermediate states. A significant contribution of the sequential mechanism for VPD from the bonded OH stretch fundamental of the donor $(000)_a + (100)_d$ to the fragments final state of one-quantum excitation of the bending mode of the donor or acceptor was demonstrated (See Fig. 2). Our calculations for the VPD of water dimmer are compared with the results of the quasi-classical calculations performed by Bowman's group [1, 2].

[1] L. C. Ch'ng, A.　K. Samanta, G. Czakó, J. M. Bowman, H. Reisler, J. Am. Chem. Soc. 134, 15430-15435 (2012)
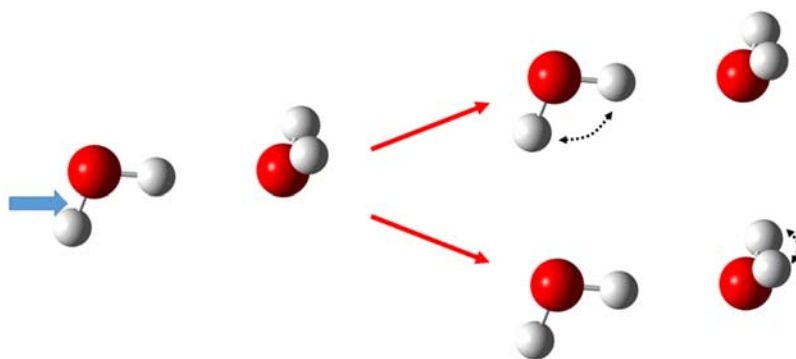[2] G. Czakó, Y. Wang, and J. M. Bowman, J. Chem. Phys. 135, 151102 (2011)

Fig. 1. The VPD process of water dimer from the bonded OH stretch fundamental of the donor $(000)_a + (100)_d$ to the fragments final state of one-quantum excitation of the bending mode of the donor or acceptor.

Intermolecular vibrational modes	1	2	3	4	5	6
Symmetry (C_s)	A"	A"	A'	A'	A'	A"
Frequency [cm^{-1}]	128	141	151	179	351	609
Reduced mass [amu]	1.0705	1.0325	1.5803	2.2927	1.0958	1.0417

Table 1. Low frequency vibrational modes of water dimer calculated by using CCSD level of theory with the basis set aug-cc-pVTZ.
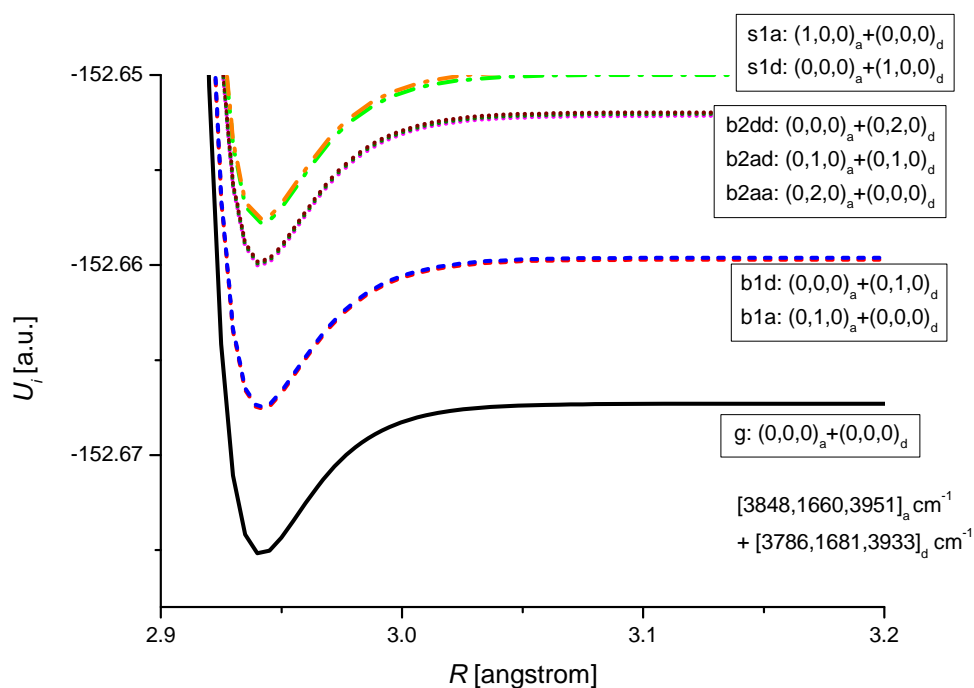

Fig. 2. Adiabatic potential energy curves along the v_5 intermolecular vibrational mode for vibrational predissociation of water dimer.