Adiabatic treatment for vibrational predissociation of water dimers with channel interactions

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Synopsis The results of calculated vibrational predissociation (VPD) of water dimers are presented. The VPD processes considered here are the followings: initially closed channel of symmetric stretching mode is excited by one quantum, and dissociate to two open channels of the bending mode excitation by one quantum in the donor and acceptor units. The VPD rate constants are calculated in the quantum mechanical approach under the adiabatic approximation. The channel interactions were taken into account in and between the initial and final states. The results obtained by quantum-mechanical approach are compared with both experimental and semi-classical trajectory calculation results.

Infrared-induced vibrational predissociation (VPD) 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 VPD rate constant is difficult. Therefore, the water dimer is expected to play an important role as a smallest water cluster to study the dynamics of VPD. However, the vibrational predissociation mechanism of hydrogen bonding water cluster is less understood at present stage.

The vibrational modes of the donor and accepter H_2O units of water dimer were grouped to high-frequency degrees of freedom which are localized in the donor or acceptor units, and the intermolecular modes were grouped to the low frequency-degrees of freedom in the adiabatic description.

We consider three VPD processes of water dimers $(H_2O)_2$ and $(D_2O)_2$ from the initial channel of the one-quantum excitation of the totally symmetric OH (OD) vibration in the donor water unit, $(1\ 0\ 0)_d + (0\ 0\ 0)_a$ to the two open channels of the bending-mode one-quantum excitation in the donor and acceptor water units, $(0\ 1\ 0)_d + (0\ 0\ 0)_a$ and $(0\ 0\ 0)_d + (0\ 1\ 0)_a$, respectively, and the other is to the open channel of the ground-state water dimer, $(0\ 0\ 0)_d + (0\ 0\ 0)_a$. Subscripts "a" and "d" denote the acceptor and donor water units respectively. $(l\ m\ n)$ specifies the quantum numbers of the totally symmetric stretching, bending, and anti-symmetric stretching modes respectively.

The corresponding VPD rate constants were calculated in the non-Condon scheme beyond the so-called Condon approximation. The VPD is induced by the breakdown of the vibrational adiabatic approximation and the two types of the nonadiabatic coupling matrix elements are involved: the VPD induced by the low-frequency dissociation mode and VPD of the other one through the channel interactions induced by the low-frequency vibrational modes. The channel interactions in the initial and/or final stages were taken into account.

The calculated VPD rates of the $(H_2O)_2$ are slow compared with those of the $(D_2O)_2$ for the case in which the channel interactions were omitted, while these are comparable order for the case in which the channel interactions were taken into account. The results are also compared with the results of the quasi-classical calculations and experimental results [1, 2].
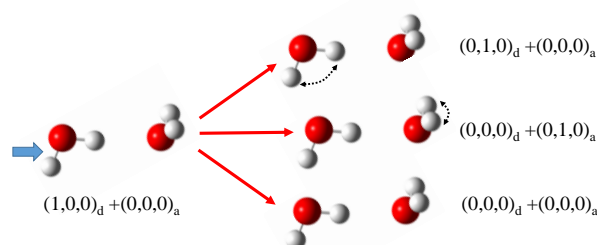

Figure 1. Vibrational VPD of water dimers from the initial channel $(1\ 0\ 0)_d + (0\ 0\ 0)_a$ to the final channels: $(0\ 1\ 0)_d + (0\ 0\ 0)_a$, $(0\ 0\ 0)_d + (0\ 1\ 0)_a$ and $(0\ 0\ 0)_d + (0\ 0\ 0)_a$, are depicted.

References

[1] L. C. Ch'ng, A. K. Samanta, G. Czakó, J. M. Bowman, H. Reisler, 2012 *J. Am. Chem. Soc.* **134** 15430.

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