

Imaging the vibrational predissociation of Ar-tagged protonated water clusters

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Introduction

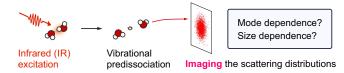
Vibrational energy transfer in the condensed phase



Inoue et al., Nat. Commun. 11, 5344 (2020).

Intermolecular vibrational dynamics

Gas phase molecular cluster as a microscopic model system



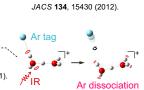
Ion imaging experiments for infrared predissociation

- Previous study: Neutral clusters
- Pioneering works by Prof. Reisler group Recent review: Acc. Chem. Res. 47, 2700 (2014).



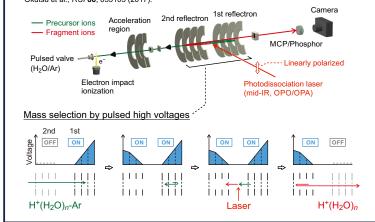
- This study: Ionic clusters

- Complete cluster size selection ---using a home-built imaging apparatus
- Our recent paper: J. Chem. Phys. 154, 174301 (2021). (Infrared photodisssociation imaging of H2O+-Ar)



Experiment: Photofragment ion imaging

Imaging apparatus with a linear tandem reflectron TOF mass spectrometer Okutsu et al., RSI 88, 053105 (2017).

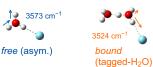


This study

Infrared photodissociation imaging of H+(H2O)1,2-Ar IR spectra were reported in Headrick et al., Science 308, 1765 (2005)

Monomer, H₃O⁺-Ar

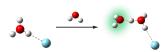
bound



Dimer, H+(H2O)2-Ar

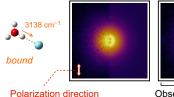


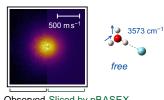
- Mode dependence? bound- vs. free-OH stretching excitation
- Size dependence? Any effect of an additional H2O molecule?



Results and discussion

Imaging result 1: H₃O⁺-Ar

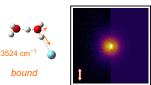




of the dissociation laser

- Observed Sliced by pBASEX Garcia et al., RSI 75, 4989 (2004).
- Isotropic → Long predissociation lifetime (> Rotational period, ~10 ps)
- Bound excitation gave a slightly larger distribution. (See the following E_t/E_{avl} plot for a clearer comparison)

Imaging result 2: H+(H2O)2-Ar

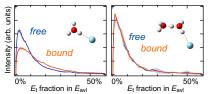






- Similar small images were observed for both modes.
 - → Translational energy did **NOT** depend on the excited vibrational modes.

 E_t/E_{avl} plot:Energy fraction into the translational energy (E_t)

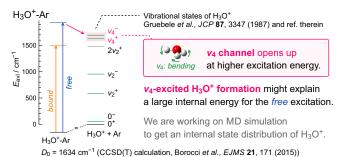


Available energy, $E_{\text{avl}} = hv - D_0$ $(D_0 = Ar-dissociation energy)$

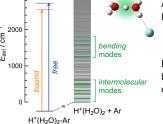
is distributed into translational (Et) and internal energy $(E_{\text{vib.}} + E_{\text{rot.}})$.

 H_3O^+ -Ar: bound > free \rightarrow Large internal energy in H_3O^+ for the free excitation $H^{+}(H_{2}O)_{2}$ -Ar: bound = free \rightarrow Little mode dependence in the E_{t} fraction

Energy diagram for vibrational predissociation



 $H^+(H_2O)_2$ -Ar An additional H₂O molecule caused low-frequency intermolecular modes.



Efficient intermolecular energy transfer between the two H₂O (H₂O-H⁺-H₂O) occurred faster than Ar predissociation.

 \rightarrow Loss of mode dependence

→ Dense vibrational states

 $D_0 = 959 \text{ cm}^{-1} \text{ (MP2/AVDZ, Douberly et al., JPCA 114, 4570 (2010))}$

Conclusion

Imaging study for the IR predissociation of mass-selected ions

- 1) H₃O⁺-Ar: Mode-dependent E_t distributions due to its discrete energetics
- 2) H⁺(H₂O)₂-Ar: Fast intermolecular energy relaxation before predissociation