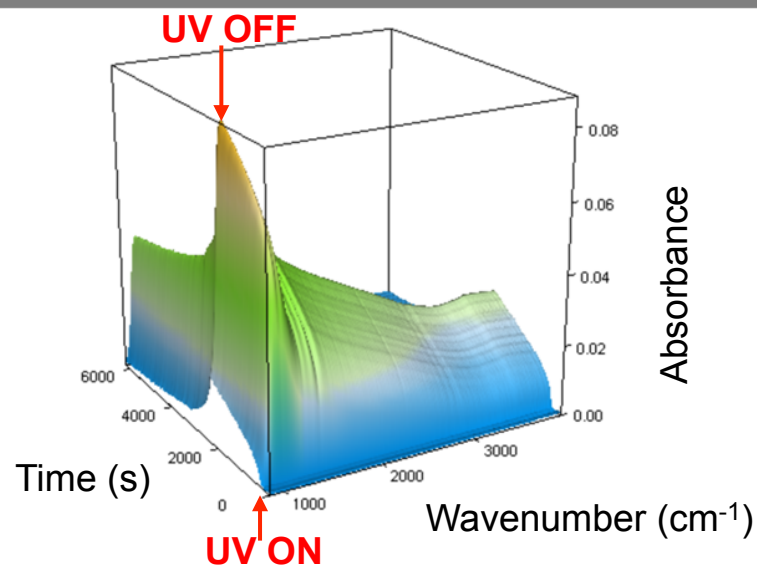
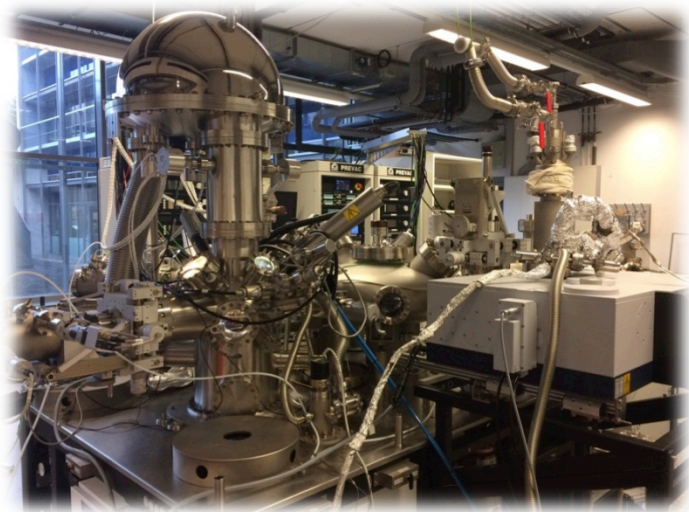


Time-resolved IR spectroscopic studies of Sr-NaTaO₃ photocatalysts

Xiaojuan Yu, Chengwu Yang, Stefan Heissler, Alexei Nefedov, Hiroshi Onishi⁺,
Yuemin Wang and Christof Wöll

Institute of Functional Interfaces, Chemistry of oxydic and organic Interfaces



I. Introduction

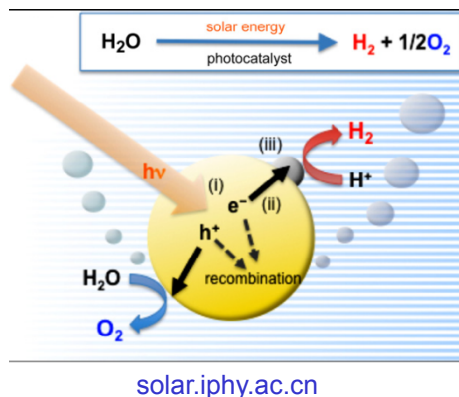
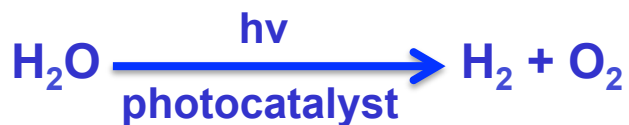
II. Experimental

III. Results

- Time-resolved IR results during UV irradiation
- Atomic H (D) doping experiments

IV. Conclusions

Introduction



NaTaO₃ perovskite structure

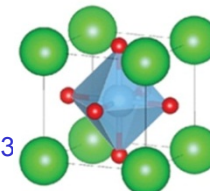
quantum yield > 50 %

La-doped NaTaO₃

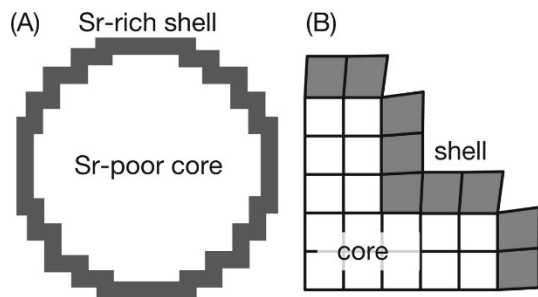
A. Kudo et al., Chem. Phys. Lett. **2000**, 331, 373

Ca, Sr, Ba-doped NaTaO₃

Iwase et al., ChemSusChem, **2009**, 2, 873.

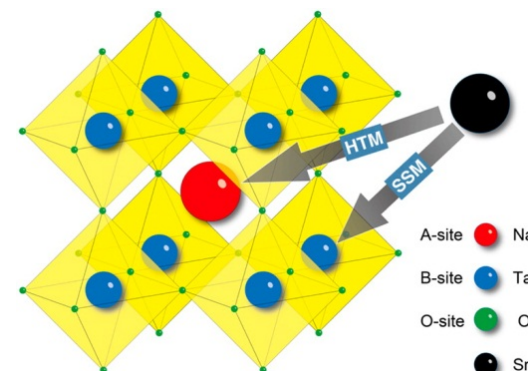


Core – shell structure



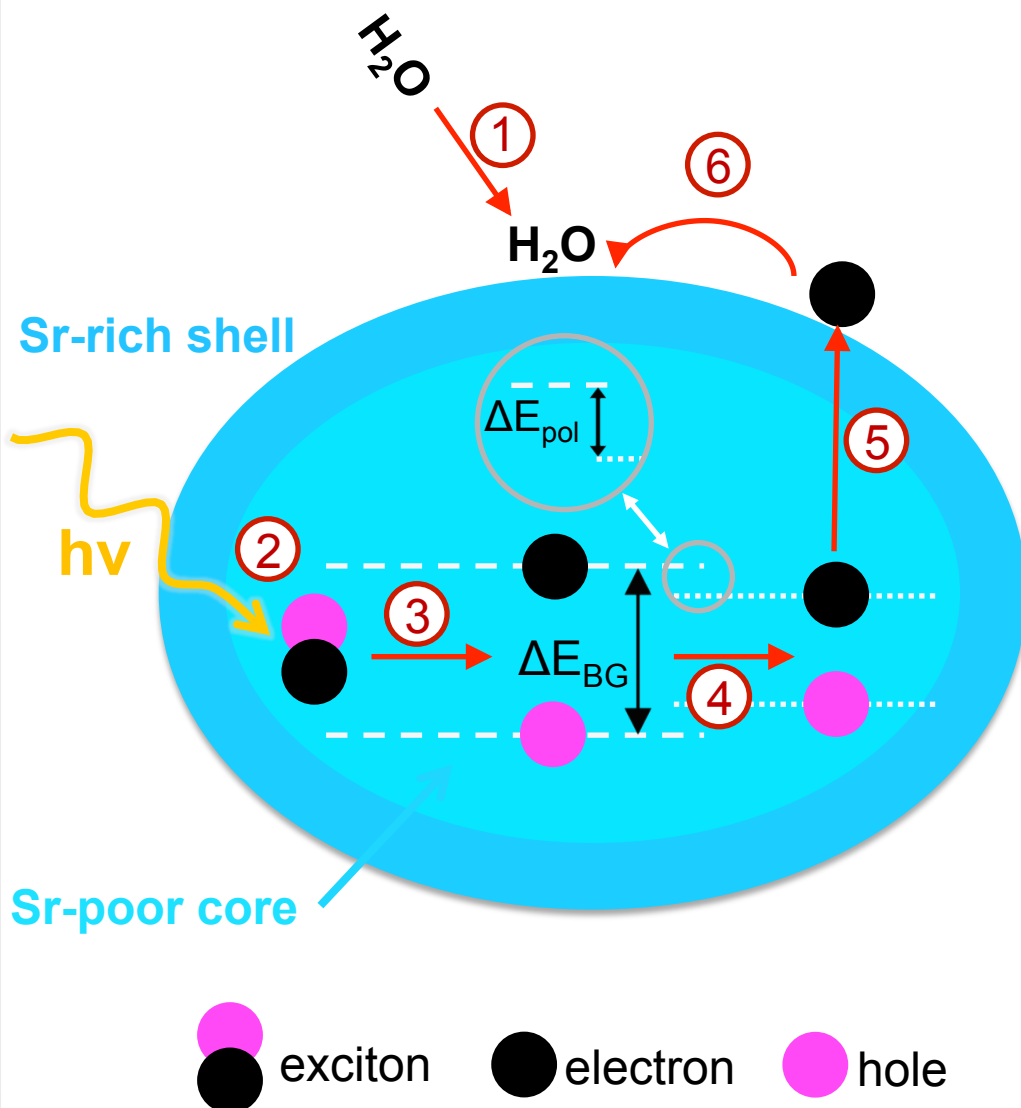
L. An et al., J. Phys. Chem. C, **2015**, 119, 28440–28447.

Sr-NaTaO₃ photocatalyst



L. An, H. Onishi, ACS Catal., **2015**, 5, 3196–3206.

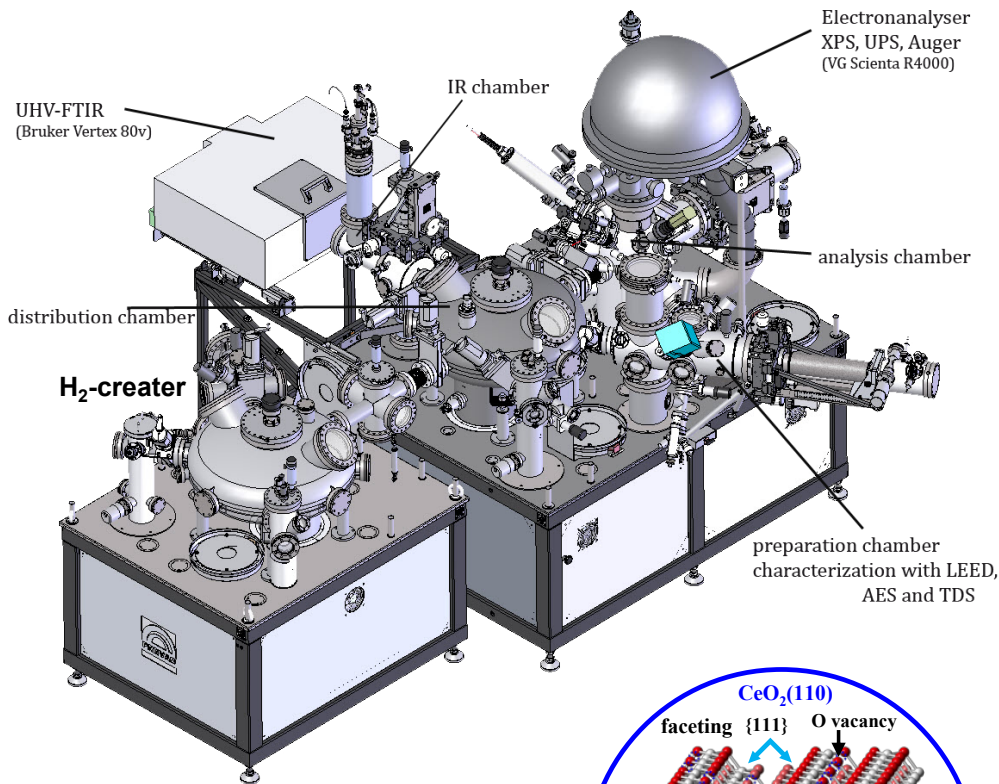
Individual Steps in a Photocatalytic Reaction



1. Adsorption of molecules on surface
2. Generation of an exciton
3. Dissociation of exciton into electron and hole
4. Trapping of charge carriers in polaronic states
5. Transport of charge carriers to surface
6. Trigger reactions in the adsorbed molecules

H. Sezen et al., Sci. Rep. 2014, **4**, 3808
 H. Sezen et al., Nat. Commun. 2015, **6**, 6901
 Deinert, J.-C., et al., Phys. Rev. Lett. 2014. **113**: 057602.
 Thomas, D.G., J. Phys. Chem. Solids, 1960. **15**: 86-96.
 Skettrup, T., Phys. Status Solidi B, 1970. **42**: 813-819.
 Linsebigler, et al., Chem. Rev., 1995. **95**: 735-758.
 Petrik, et al., JPC Letters, 2013. **4**: 344-349.
 Petrik, Kimmel, Phys. Chem. Chem. Phys., 2014. **16**: 2338-2346.
 Thompson, Yates, Topics in Catalysis, 2005. **35**: 197-210.

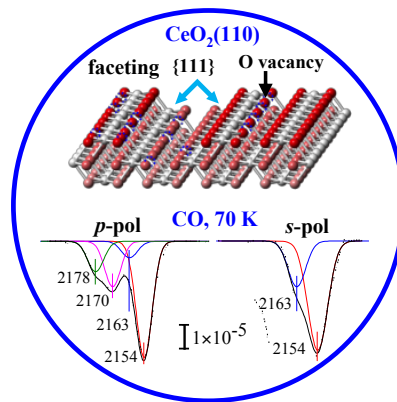
Experimental



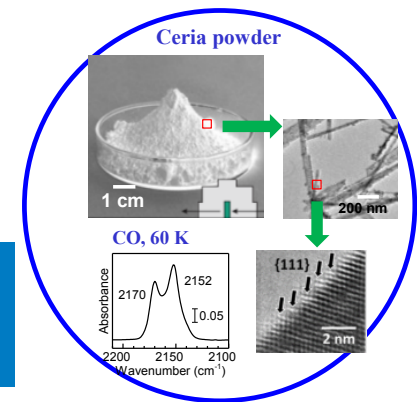
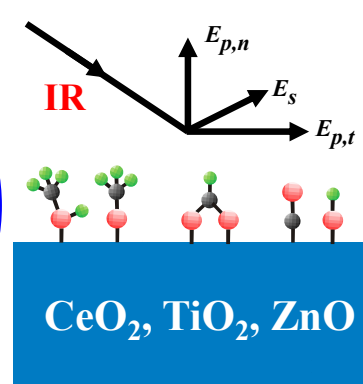
- HF-etched Sr-doped NaTaO₃
- Un-etched Sr-doped NaTaO₃
- Pure un-doped NaTaO₃

- ### IR-Measurements
- Pressure: $\leq 1 \times 10^{-10}$ mbar
 - p- and s- polarization
 - Transmission mode
 - Time-Resolution: 100 ms (rapid-scan experiments)

Yuemin Wang and Christof Wöll,
Chem. Soc. Rev. **2017**, 46,
 1875-1932.



Single crystals



Nanoparticles

I. Introduction

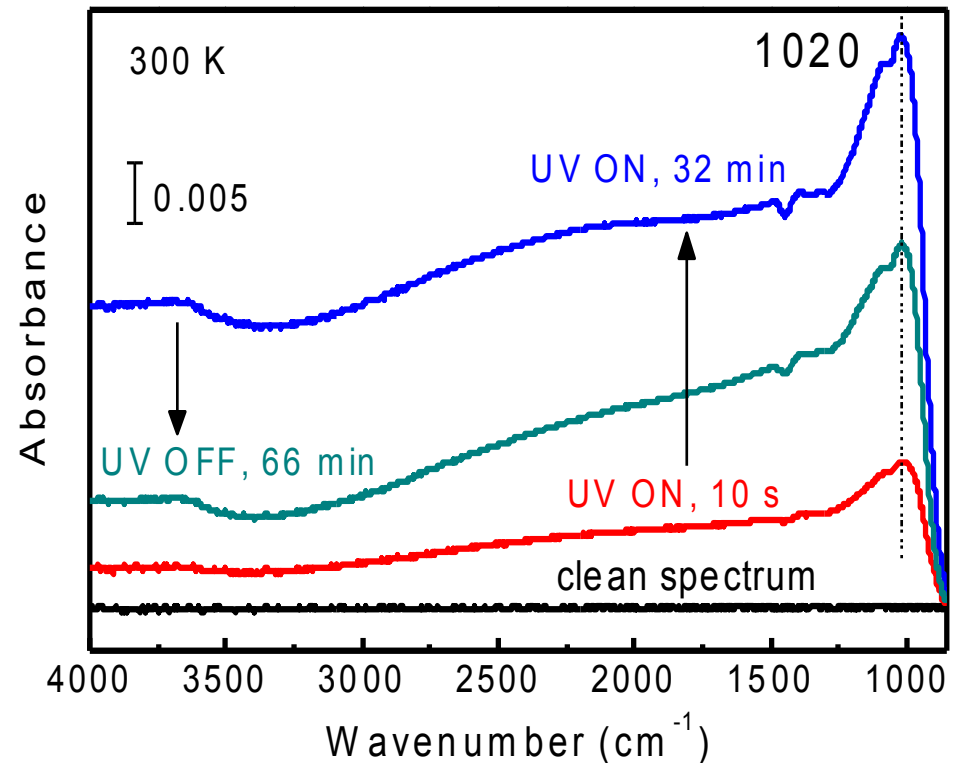
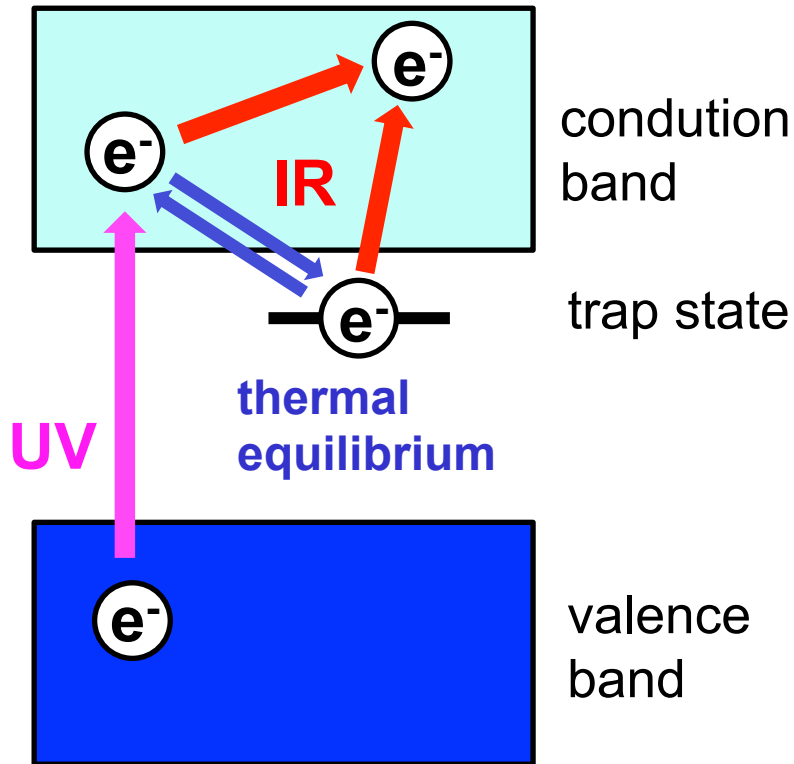
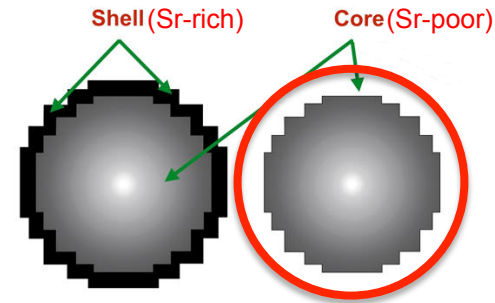
II. Experimental

III. Results

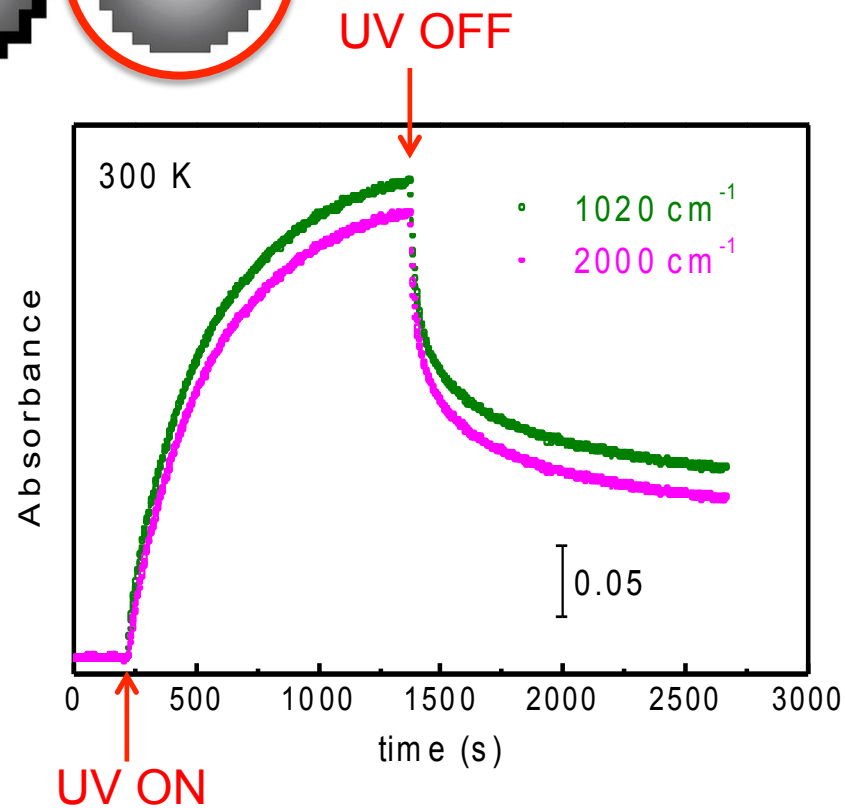
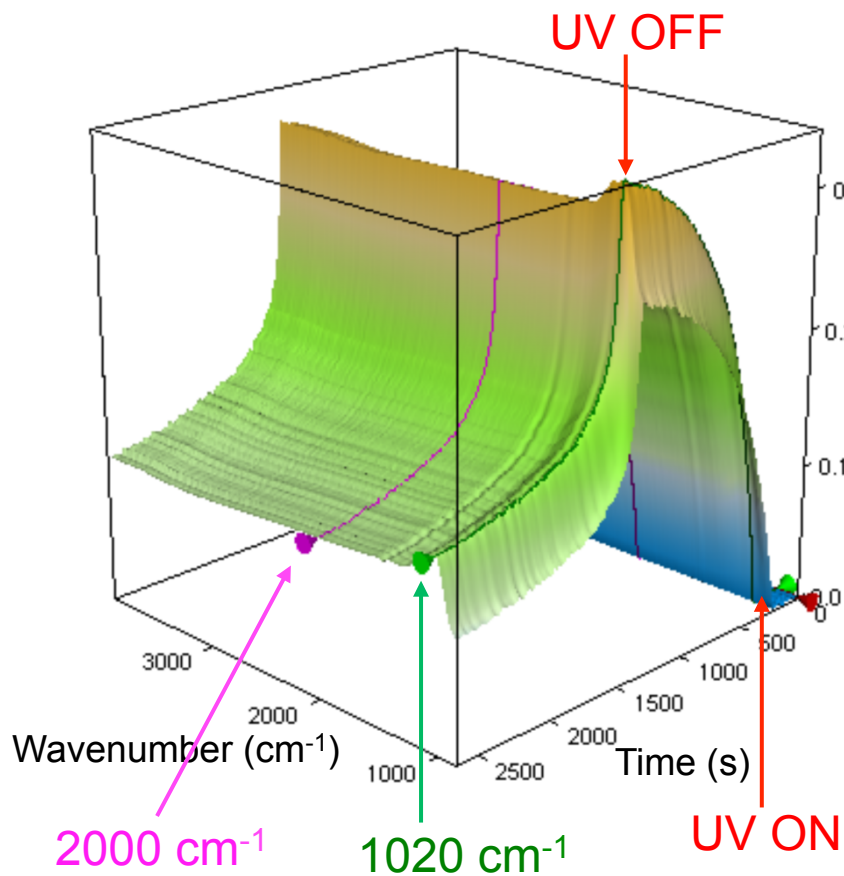
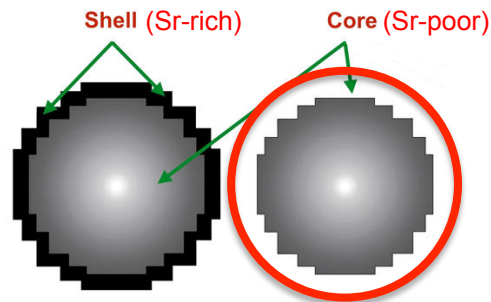
- Time-resolved IR results during UV irradiation
- Atomic H (D) doping experiments

IV. Conclusions

HF-etched Sr-NaTaO₃

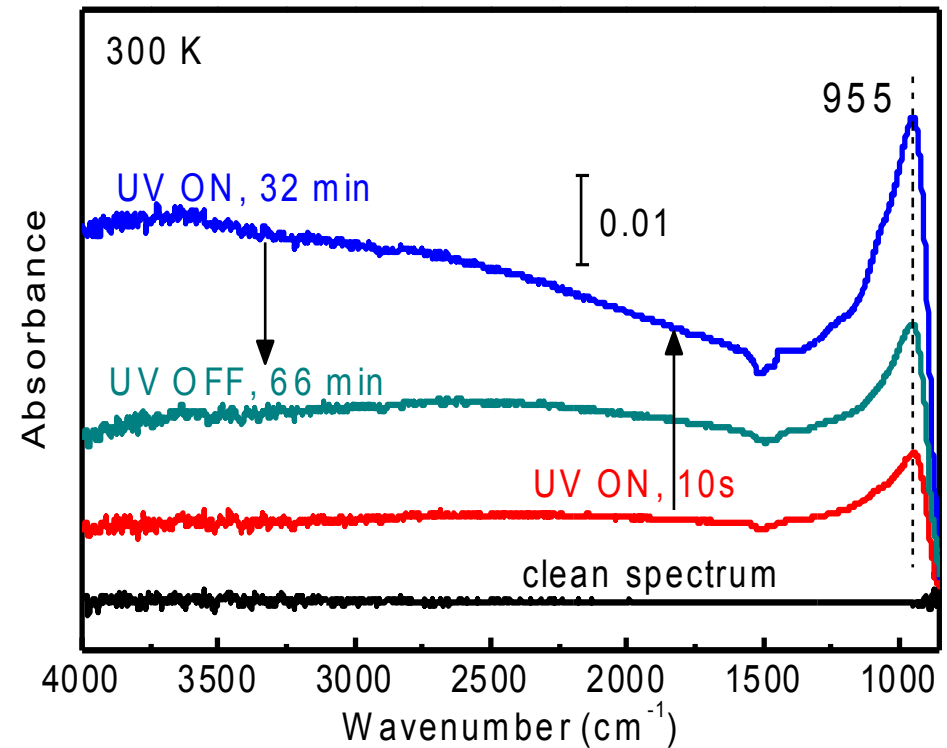
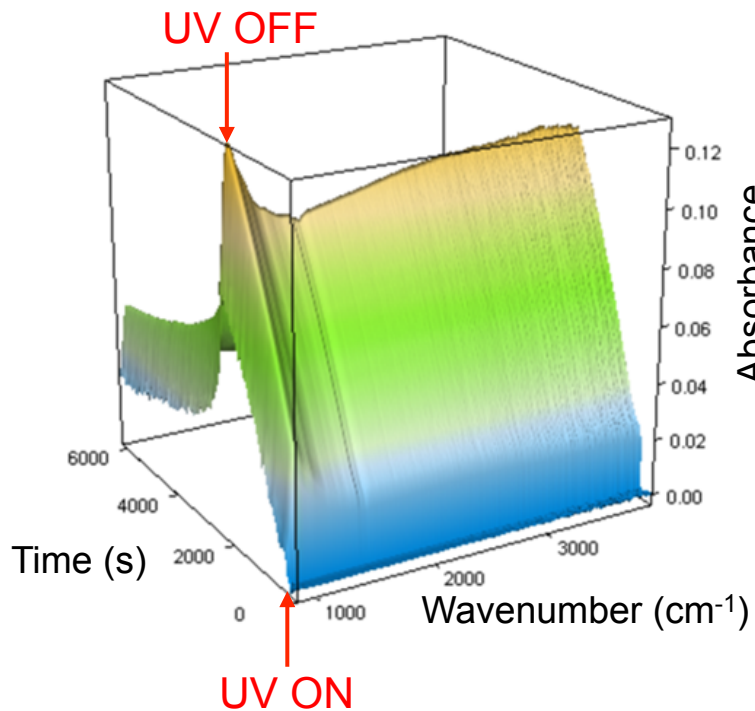
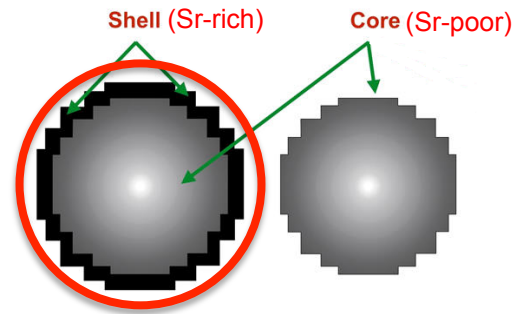


HF-etched Sr-NaTaO₃

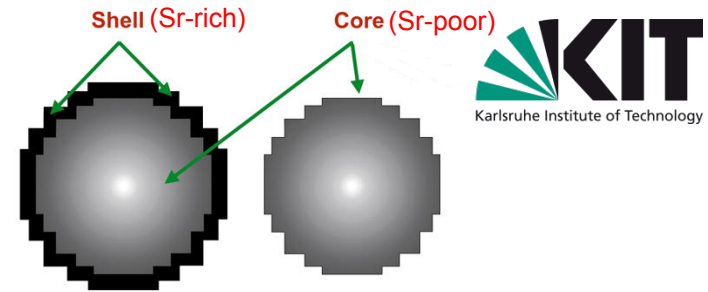


- Time-dependence for the whole spectra is the same
- Time step: 2.2 seconds per spectrum

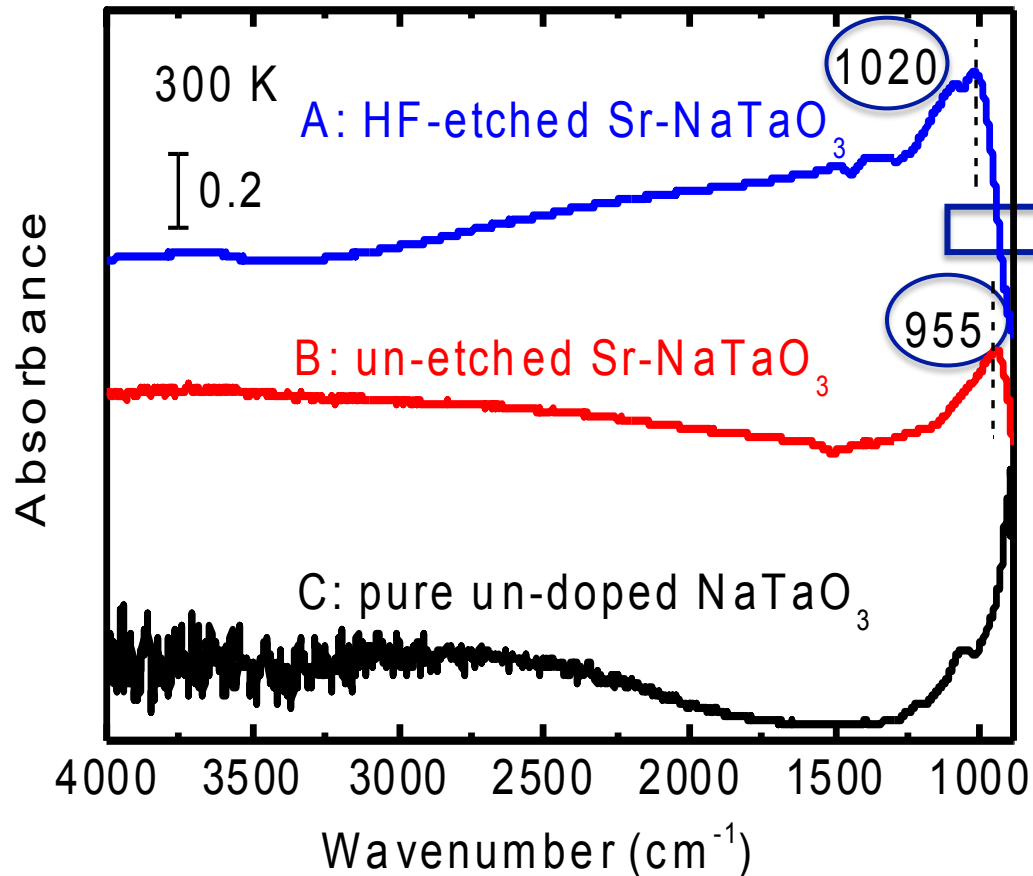
Un-etched Sr-NaTaO₃



Comparison of different samples



UV irradiation for 32 min



➤ **Vibrations ?**

➤ **Hole polarons ?**

H. Sezen et al., Nat. Commun. 2015, 6, 6901

➤ **Electron polarons ?**

H. Sezen et al., Sci. Rep. 2014, 4, 3808

I. Introduction

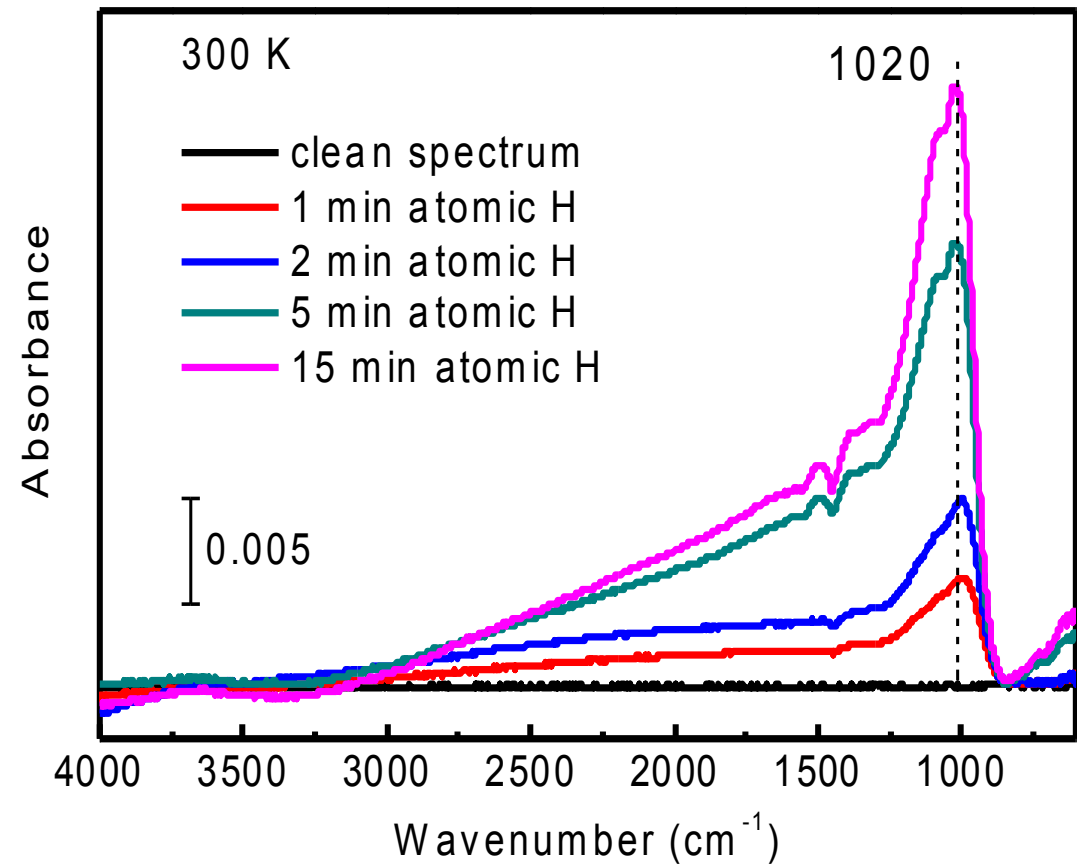
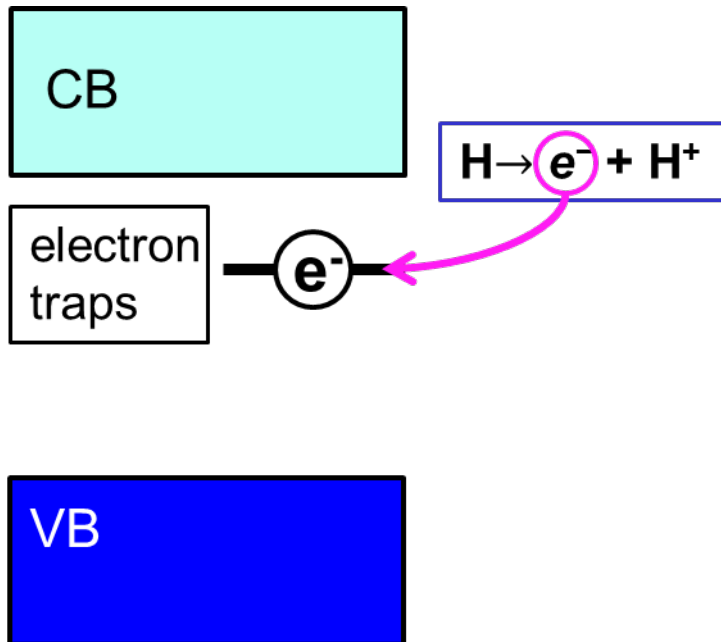
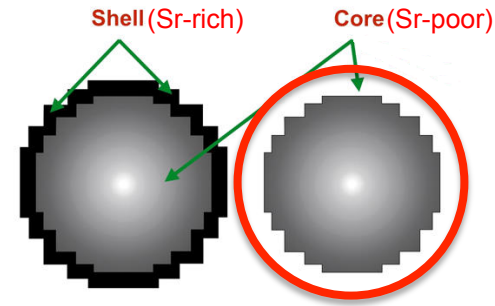
II. Experimental

III. Results

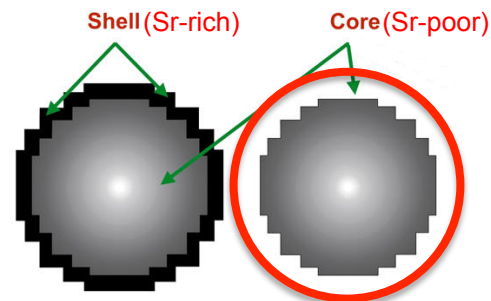
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IV. Conclusions

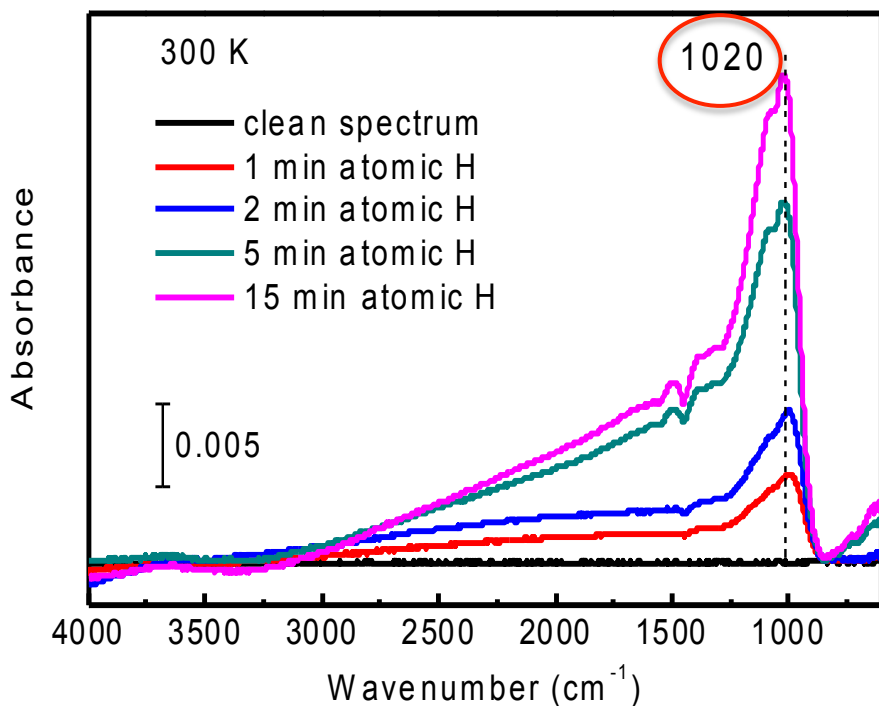
HF-etched Sr-NaTaO₃



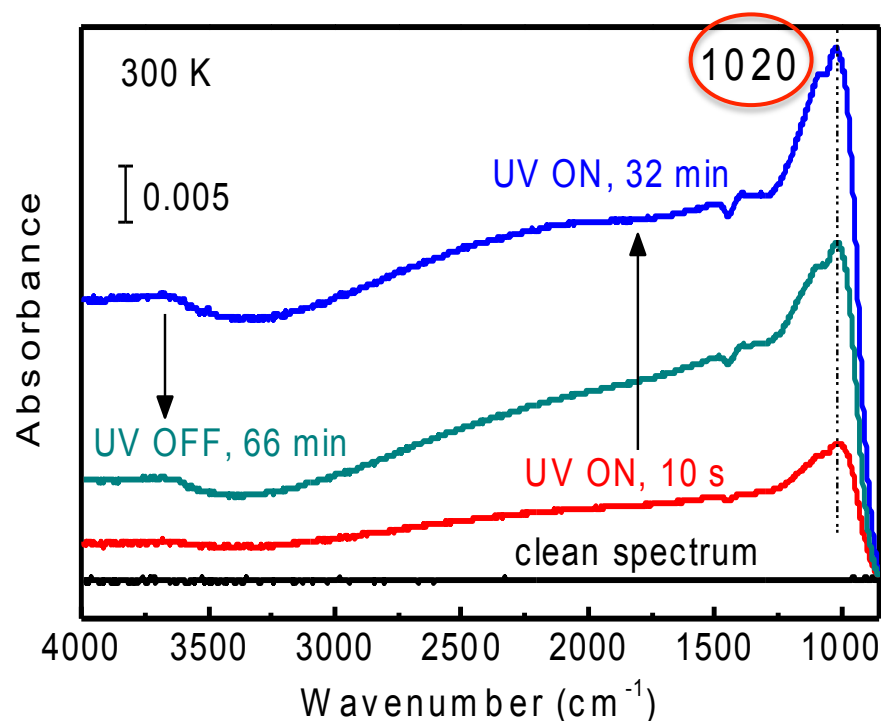
HF-etched Sr-NaTaO₃



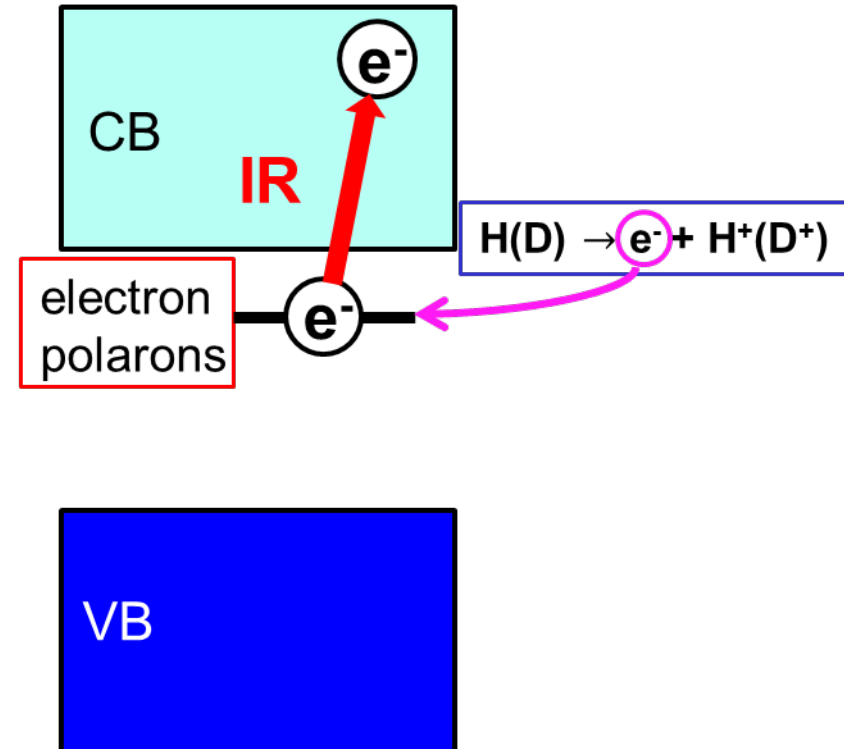
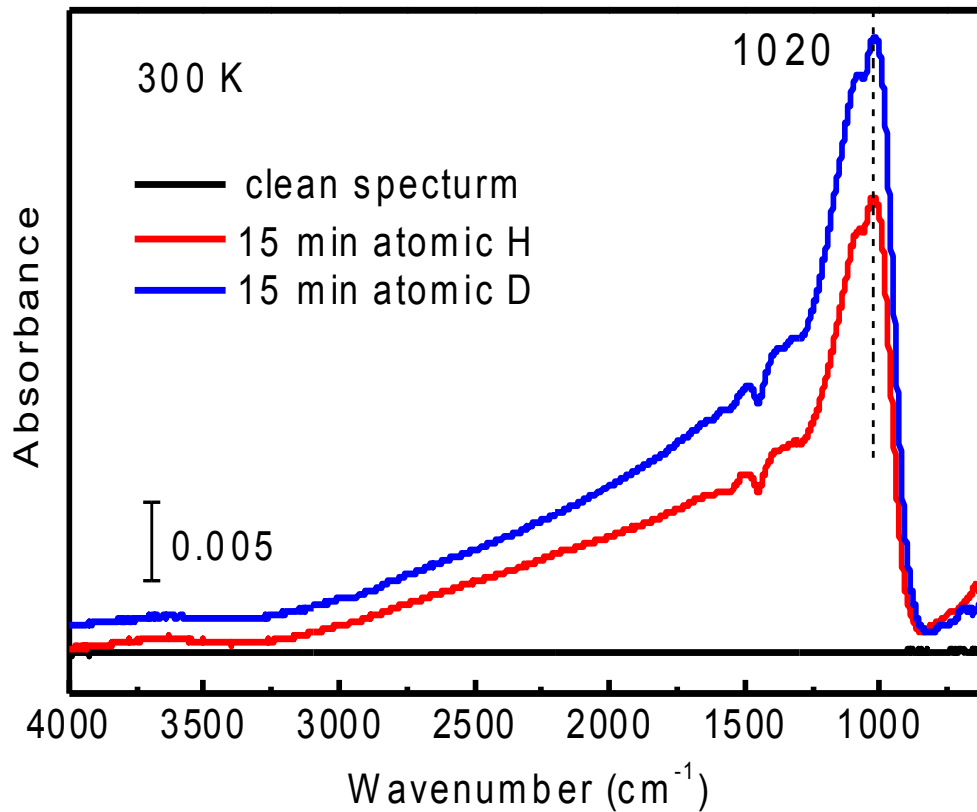
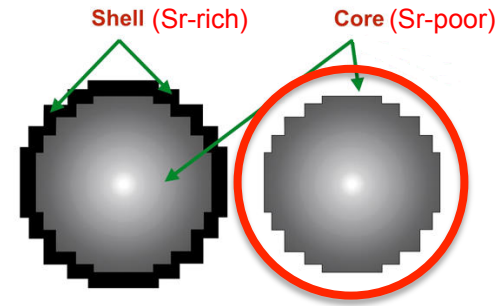
Atomic hydrogen doping



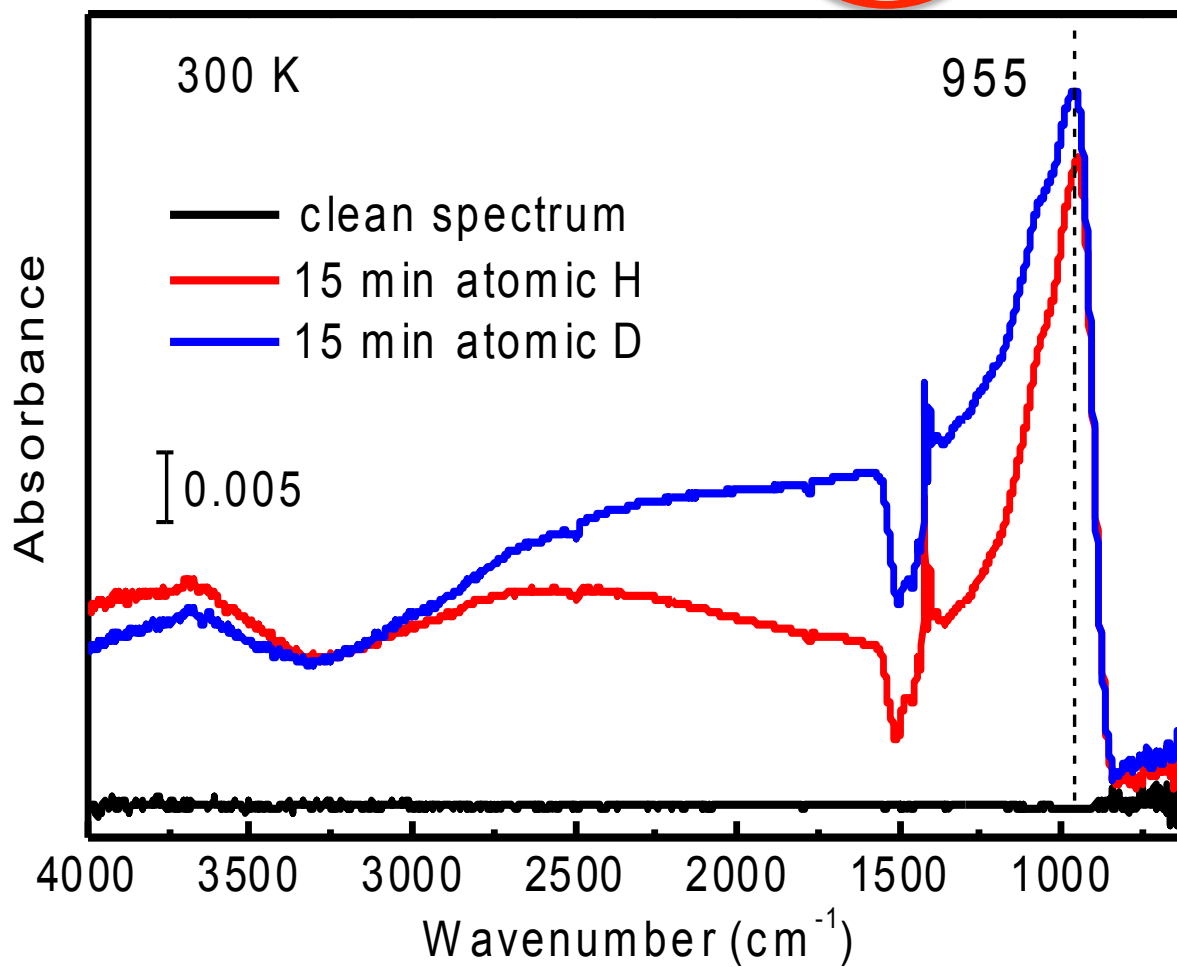
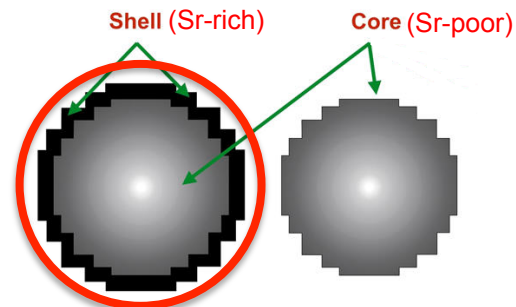
UV irradiation



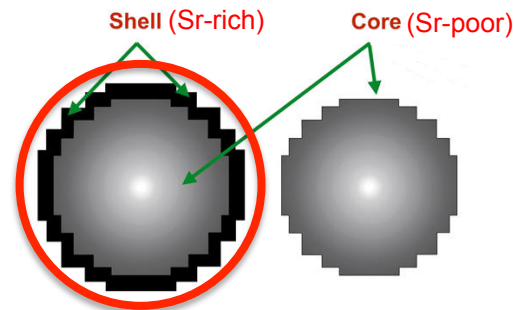
HF-etched Sr-NaTaO₃



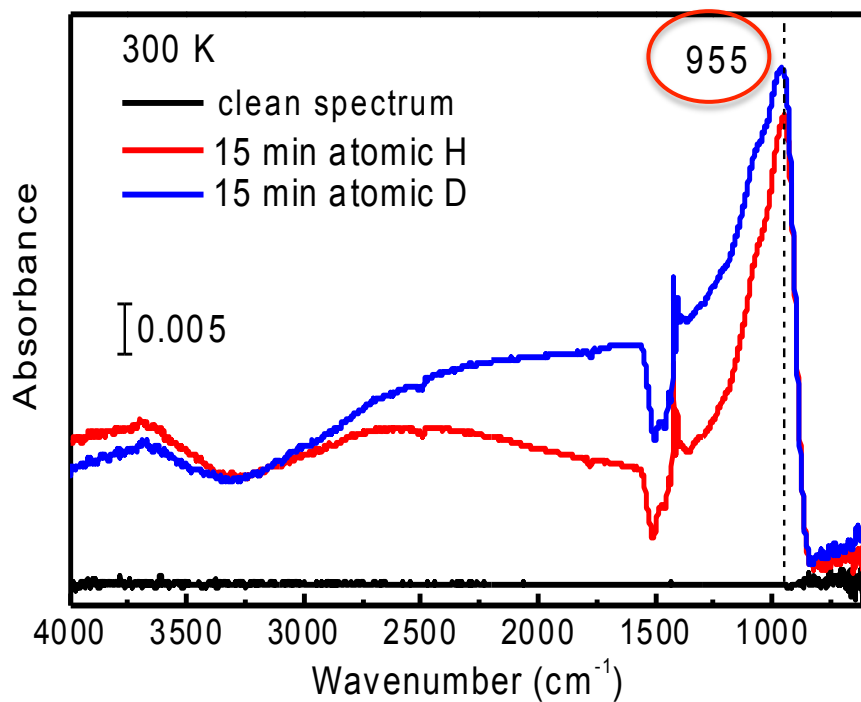
Un-etched Sr-NaTaO₃



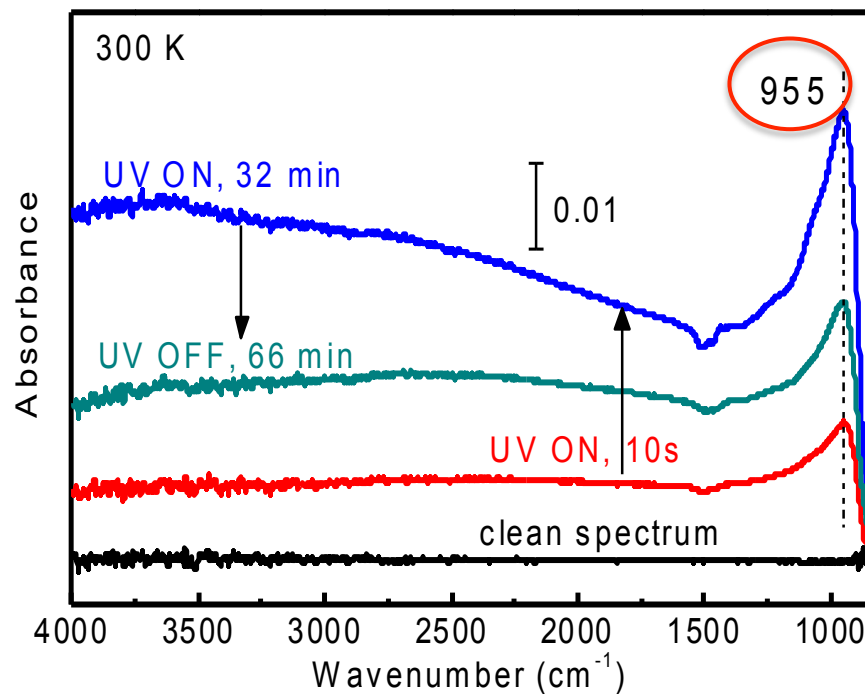
Un-etched Sr-NaTaO₃



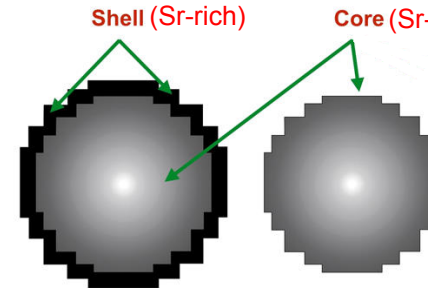
Atomic H or D doping



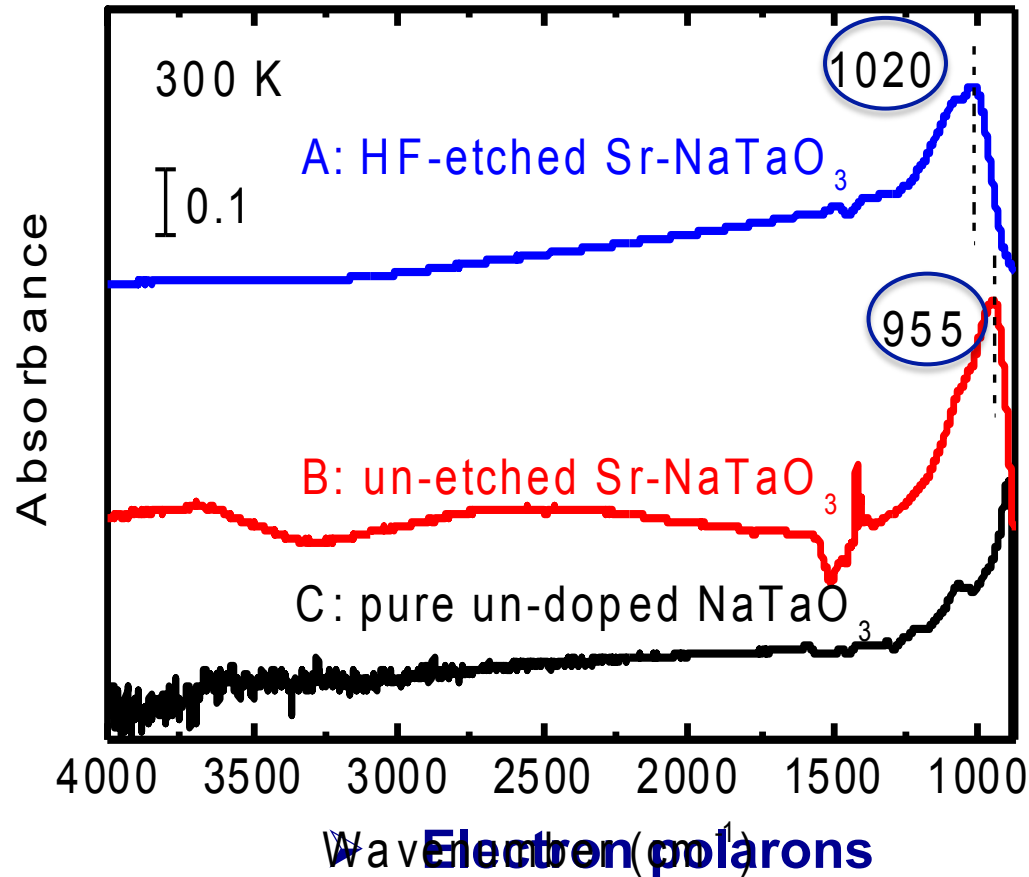
UV irradiation



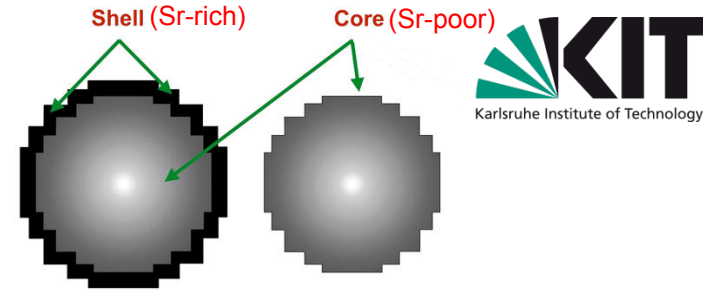
Comparison of different samples



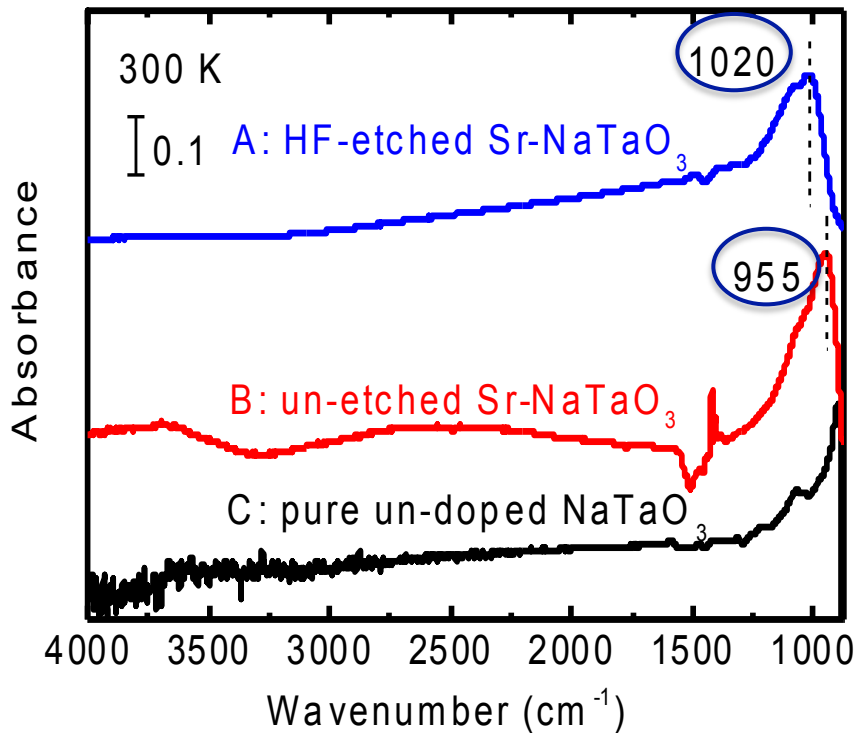
Exposure to atomic H for 15 min



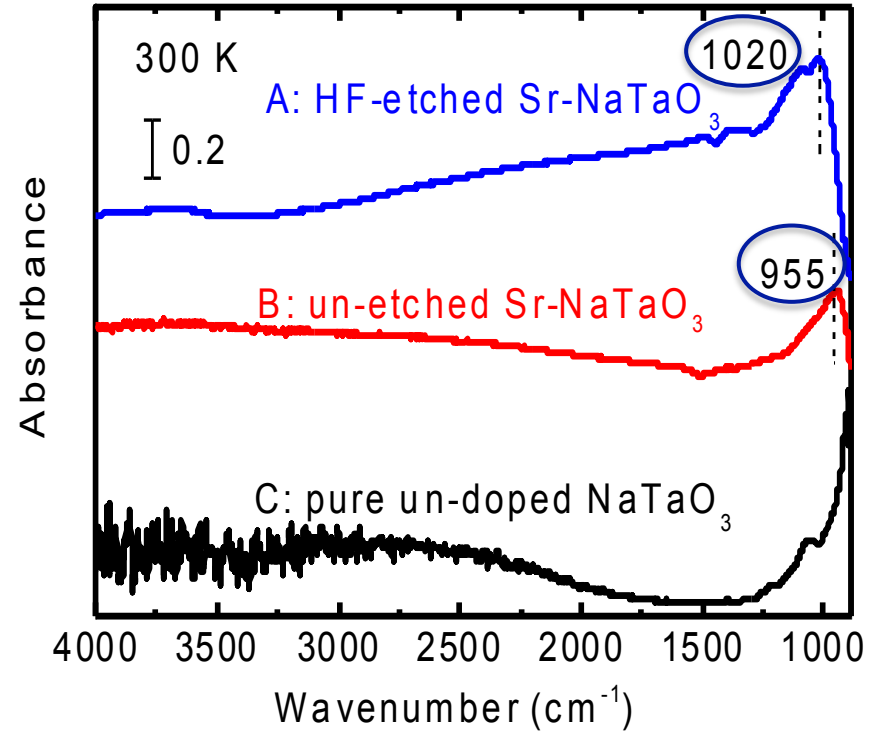
Comparison of different samples



Atomic hydrogen doping



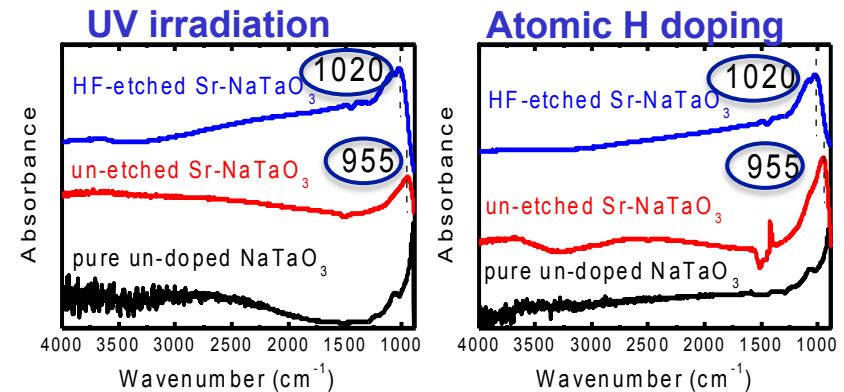
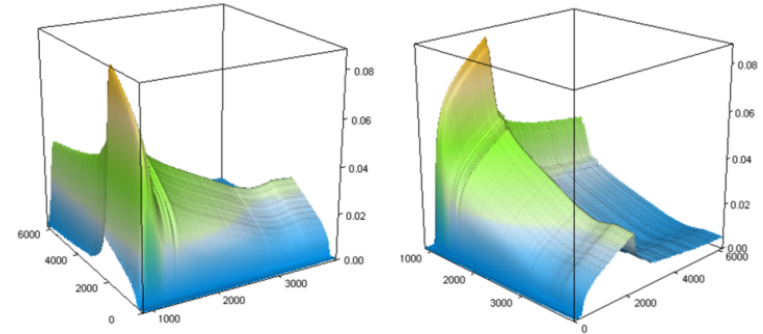
UV irradiation



➤ **Electron polarons**

Conclusions

- **Time-resolved IR spectroscopy** is suitable to study photocatalytic powder samples.
- The HF-etched and un-etched **Sr-doped NaTaO₃** samples exhibit the photocatalytic activity, whereas the pure sample is inactive.
- Based on the atomic H(D) experiments, the high photocatalytic activity of Sr-doped samples is attributed to the formation of different **electron polaron states** (HF-etched Sr-NaTaO₃: 1020 cm⁻¹; un-etched Sr-NaTaO₃: 955 cm⁻¹).



Thank you for your attention!