Infrared spectroscopy as a compliment to X-ray diffraction for zeolite examination

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Abstract

X-ray diffraction is commonly used to examine zeolite structure, but it is unable to see small changes in the long- or short-range structure. Infrared spectroscopy is used to examine changes in the long- and short-range structure of zeolite.

Structural changes in zeolite CIT-6 and derivatives upon chemical treatment are identified with mid- and far-infrared spectroscopy. Differences in the local structure of the sample are observed in the mid- and far-infrared spectra.

Zeolites

- Molecular sieve
  - Regular crystalline structure
  - Composed to TO_4 tetrahedra
  - Change uses and structure by changing T-atoms
  - Structure examined with X-ray diffraction
- Widely used in industry

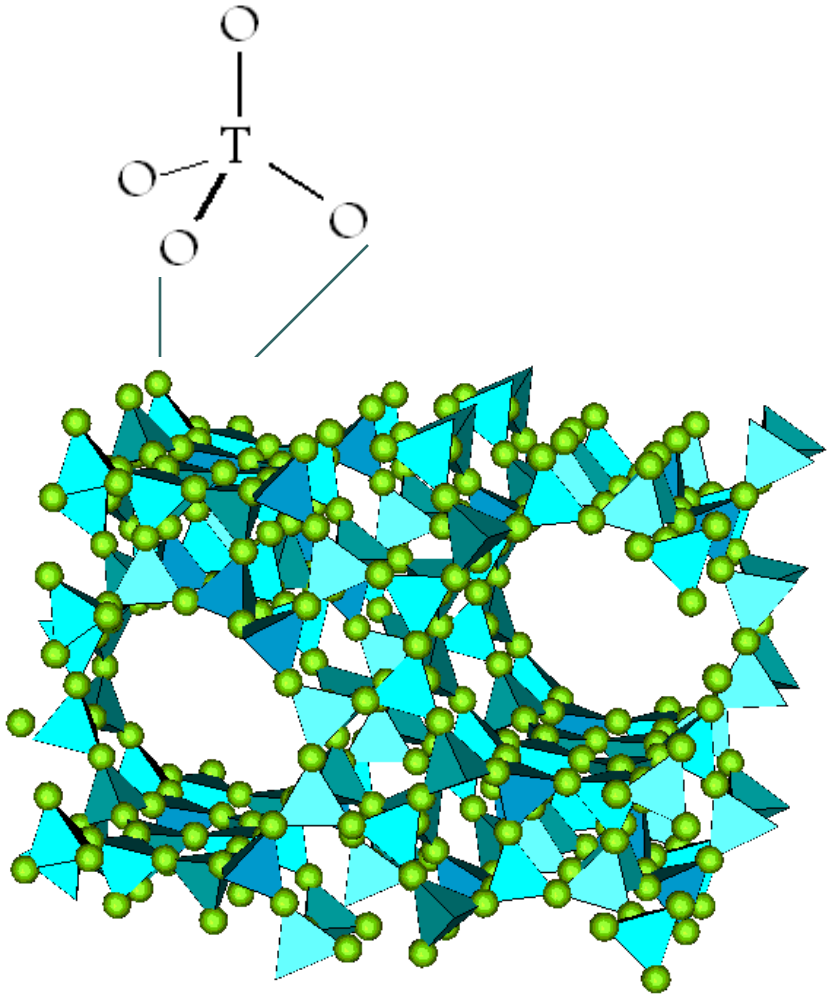


Image from: http://www.personal.utulsa.edu/~geoffrey-price/zeolite/beta-a.jpg

Zeolite structure

- X-ray diffraction (XRD) most common tool
  - Easy to use
  - Long-range structure
- See distance between layers of atoms
  - Gives structure and composition
- Short-range changes not visible with XRD

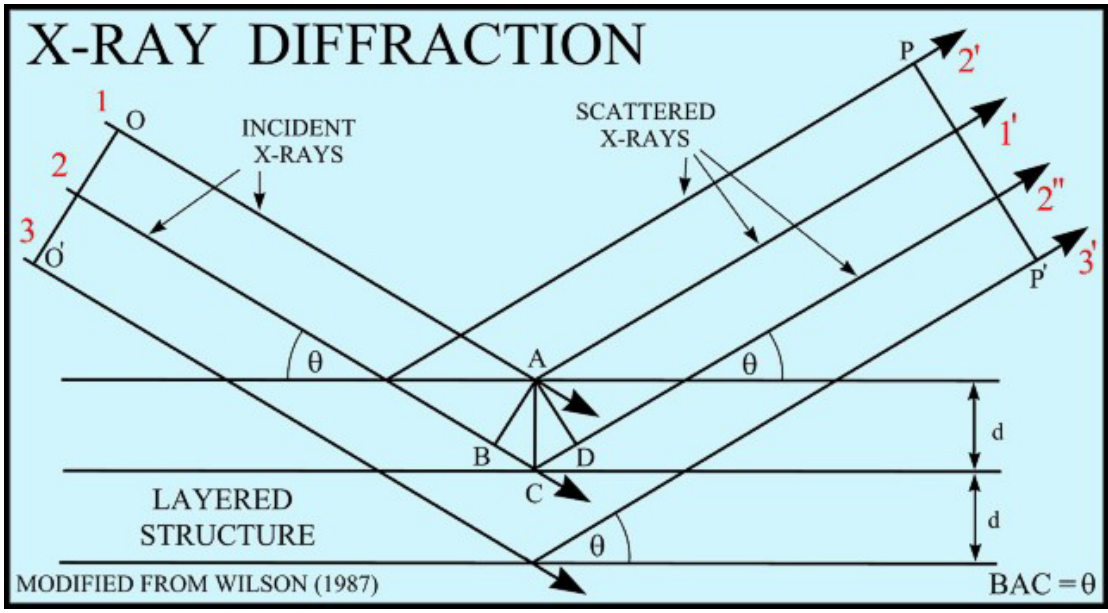
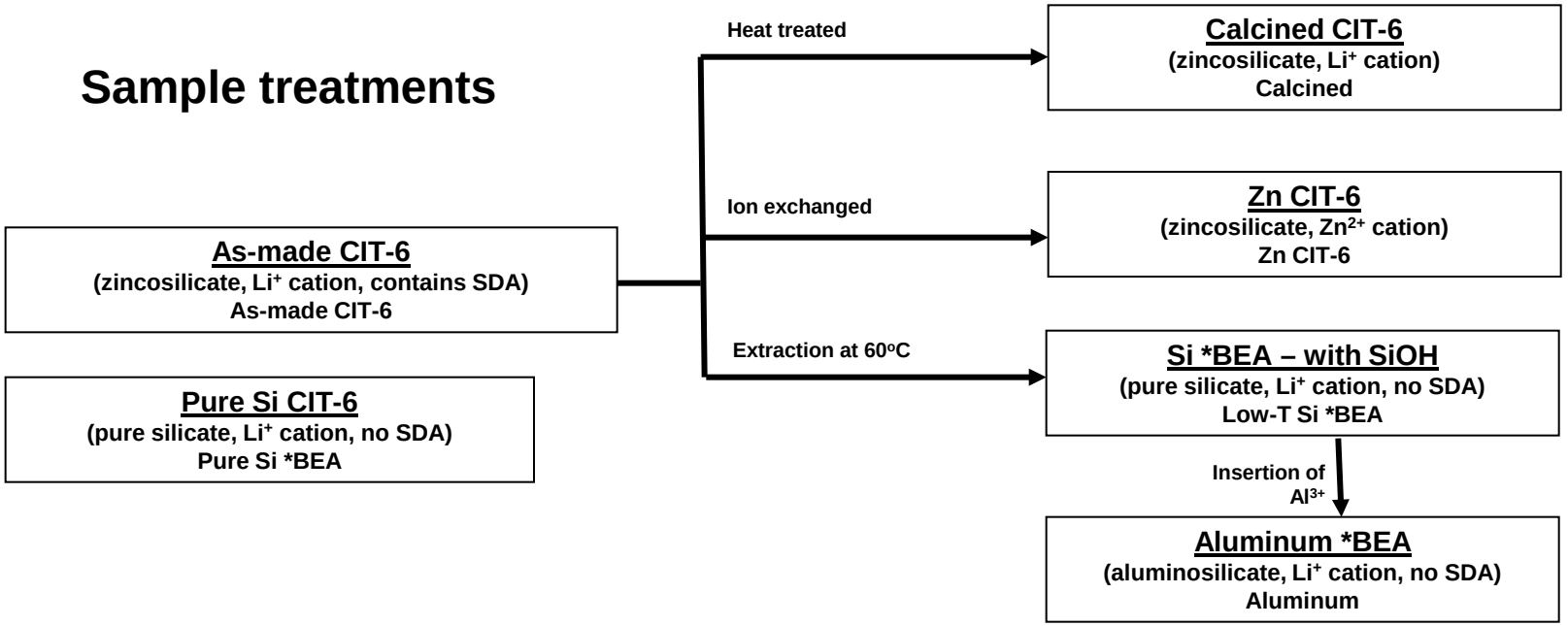


Image from: http://pubs.usgs.gov/of/2001/of01-041/htmldocs/images/beam.jpg

How to see short-range changes in structure?

- Infrared spectroscopy (IR)
  - Fourier Transform IR widely used
    - Easy to use
    - Full spectrum quickly
  - Identify atomic bonds in molecules
  - Sensitive to changes in environment
    - Composition
    - Structure

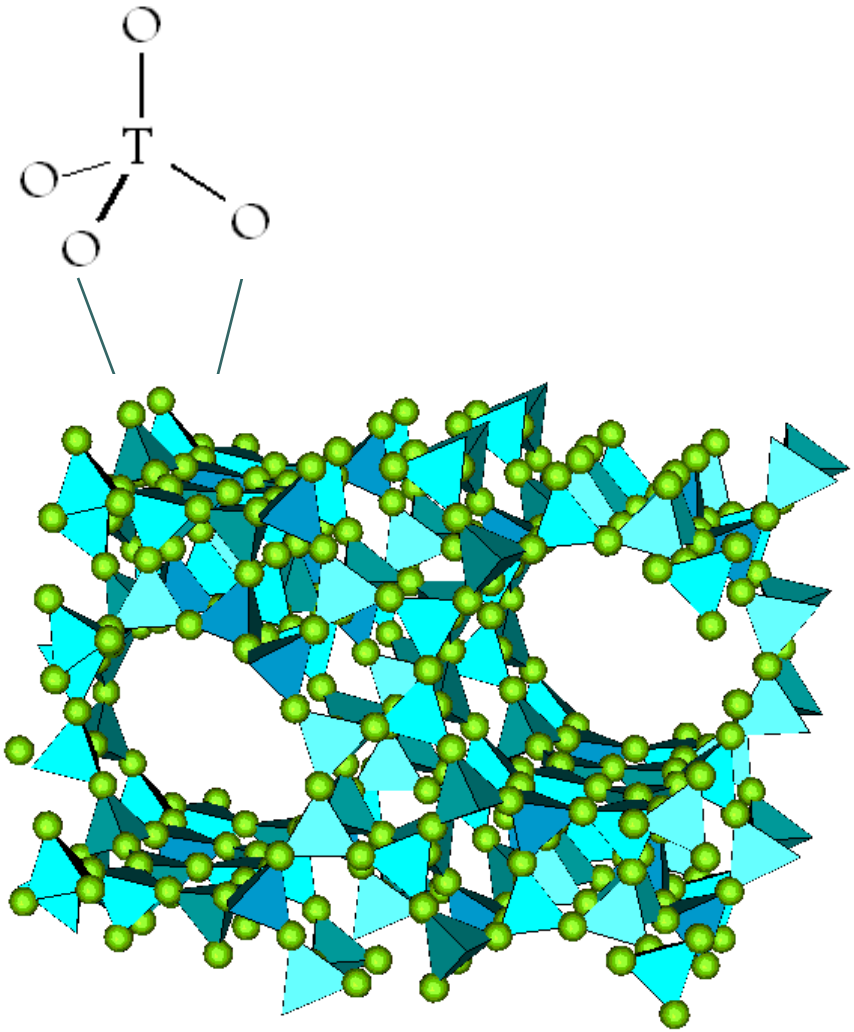
Methods



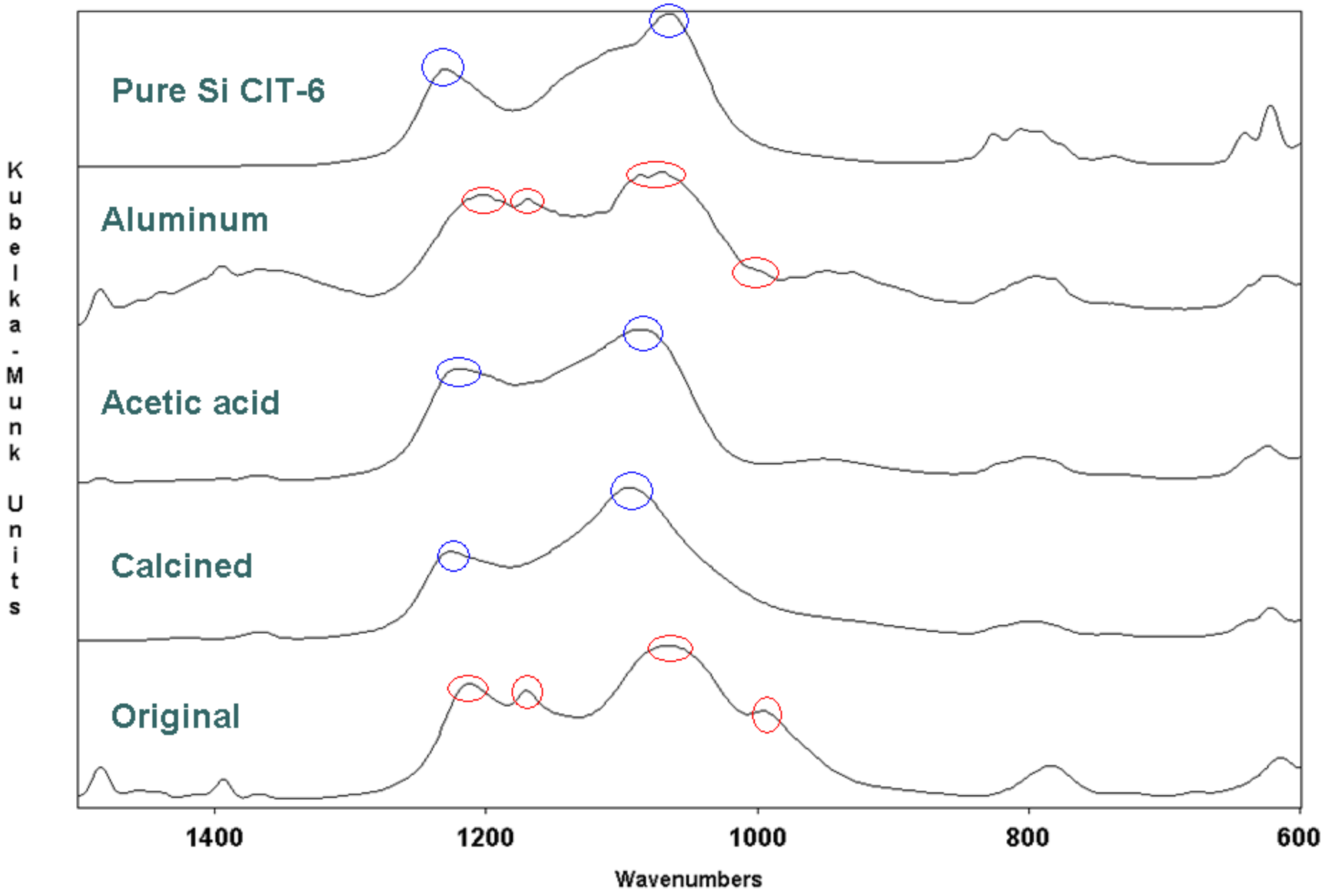
- Spectra collected with Mattson Cygnus FT-IR
  - Diffuse-reflectance IR used
  - Samples mixed with CsI at 1:5 ratio

Results – Mid-infrared

- Differences between 1250 to 975 wavenumbers
- Show changes in O-T-O stretching from treatments
  - Chemical or heating treatment of zeolite
- Short-range structure changed for Calcined and Acetic acid samples
  - More like Pure Si CIT-6
- Aluminum sample changed to be more similar to original CIT-6
- IR does see changes not visible in XRD

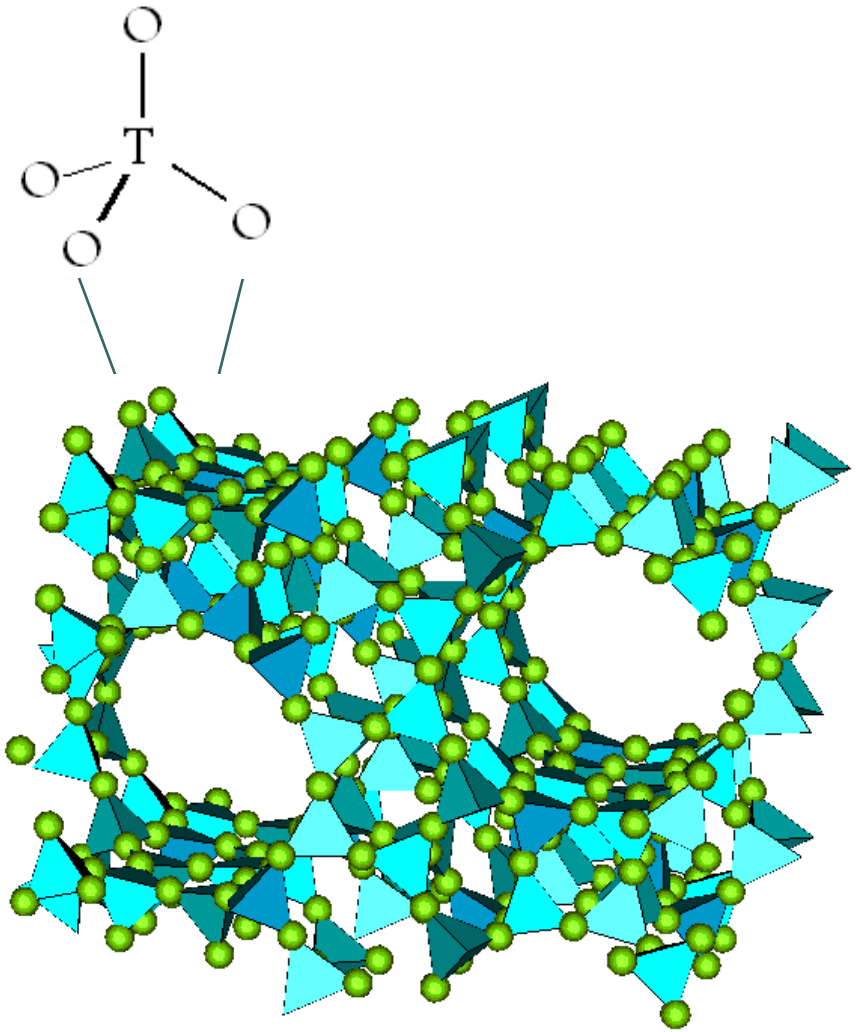


Short-range O-T-O changes

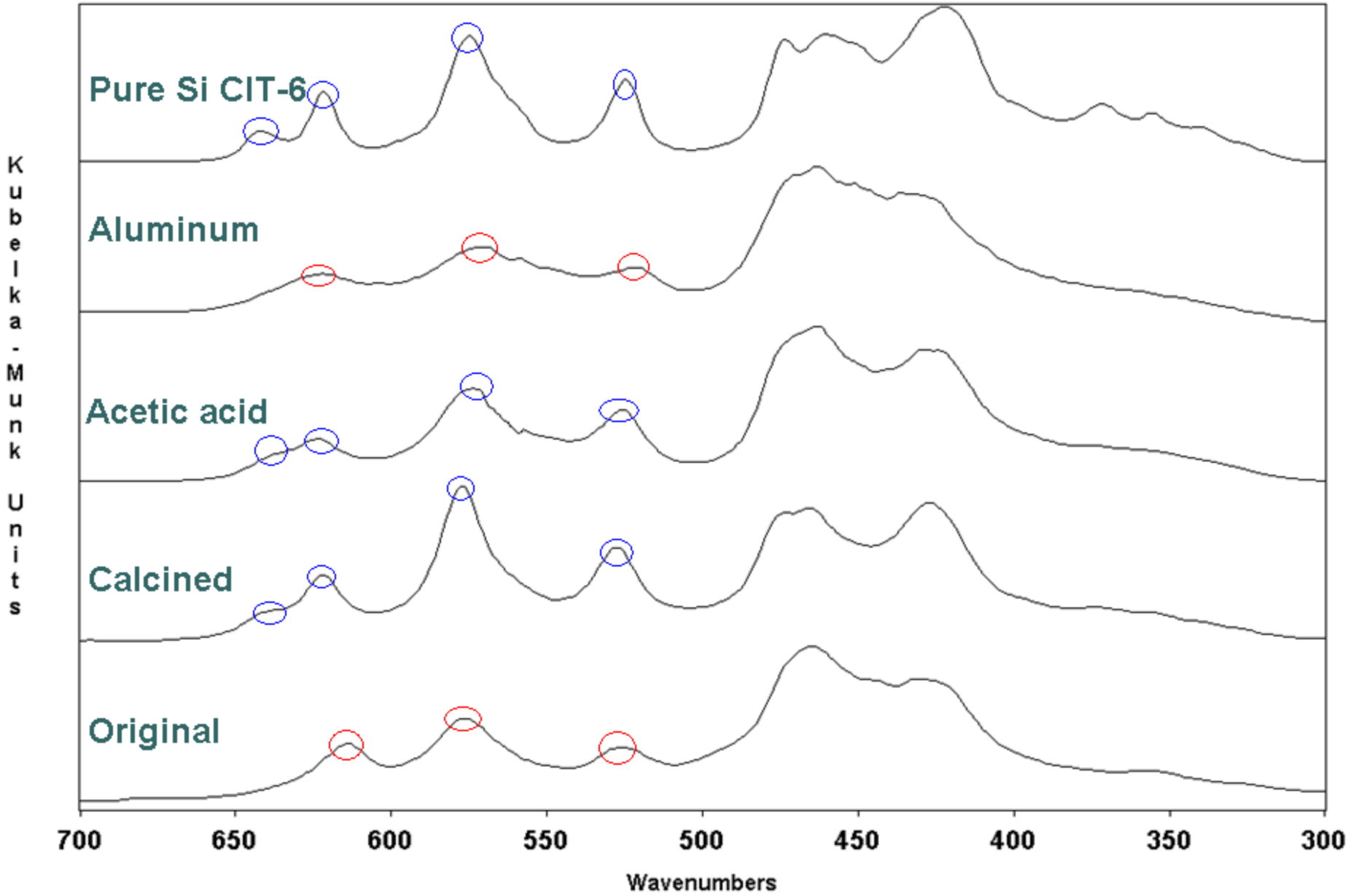


Results – Far-infrared

- Long-range
  - Double-ring modes
    - 700 to 500 cm^{-1}
- See long-range changes in zeolite
- Calcined and acetic acid samples more like Pure Si CIT-6
- Aluminum sample changes back to be more similar to Original
- IR again sees changes not visible in XRD



Long-range structure changes



Conclusions

- Mid-infrared shows evidence of short-range changes
- Far-infrared shows evidence of long-range changes
- IR a useful tool for zeolite structure examination
  - Development of new zeolites
  - Modifying existing zeolites

References

- Andy, P.; Davis, M. E. *Ind. Eng. Chem. Res.* **2004***, 43*, 2922-2928.
- Takewaki, T.; Beck, L. W.; Davis, M. E. *Top. Catal.* **1999***, 9*, 35-42.
- Takewaki, T.; Beck, L. W.; Davis, M. E. *J. Phys. Chem. B* **1999***, 103*, 2674-2679.
- Camblor, M. A.; Corma, A.; Valencia, S. *Chem. Comm.* **1996**, 2365.
- Flanigen, E. M.; Khatami, H.; Szymanski, H. A. *Adv. Chem. Ser.* **1971***, 101*, 201-229.
- Flanigen, E. M. *ACS Monograph* **1976***, 171*, 80-117.
- Socrates, G. In *Infrared Characteristic Group Frequencies;* John Wiley & Sons: Chichester, 1994; , pp 249.

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