Supporting Information for:

Spatially Resolved Imaging of Inhomogeneous Charge Transfer Behavior in Polymorphous Molybdenum Oxide.

I. Correlation of Localized Structural, Electronic, and Chemical Properties Using Conductive Probe AFM and Raman Microprobe Spectroscopy

Todd M. McEvoy^{\dagger} and Keith J. Stevenson*

*Contribution from the Department of Chemistry and Biochemistry, Center for Nano- and Molecular Science and Technology, Texas Materials Institute The University of Texas at Austin, Austin, Texas 78712

*Corresponding author: Fax 512-471-8696 *E-mail address*: <u>stevenson@mail.cm.utexas.edu</u>

[†] Current address: Air Products and Chemicals, Inc. 7201 Hamilton Blvd., Allentown, PA 18195

There are several known structures of molybdenum oxide (MoO_3) and depending upon preparation conditions such as chemical precurors, thin film deposition methods and heat-treatment temperature, different forms of MoO₃ can be created. The subtle differences between our electrochemically-deposited films and those prepared by other routes are crossed referenced in Table 1 and their characteristic assignments are discussed below. The α -MoO₃ phase exhibits O_h symmetry with six normal vibrational modes. From the six, only three modes, v_1 , v_2 , and v_5 are Raman-active modes whereas v_3 and v_4 are infrared-active modes.¹ The sixth mode, v_6 is neither Raman nor infrared-active. Accordingly, using the reported space group D_{2h}^{16} for the unit cell,² the expected Ramanactive vibrational modes are A_g , B_{1g} , and B_{3g} . The remaining modes, B_{1u} , B_{2u} and B_{3u} are infrared-active, while A_u is inactive.³ These symmetry operations are also included in the last column of Table 1 along with suggested physical descriptions of each stretch taken from the literature. The characteristic spectra for α -MoO₃ (Figure 3a) shows intense, unique Raman shifts at 995 and 820 cm⁻¹, while less intense peaks are found at 666, 337 and 289 cm⁻¹. The peak located at 995 cm⁻¹ is indicative of a stretch between molybdenum and a doubly bonded oxygen (Mo=O, designated as vOMo). The most intense peak of the α -MoO₃ spectrum is located at 820 cm⁻¹ and is associated with a stretching vibration involving two molybdenum atoms bonded to one oxygen atom (ν OMo₂). A weak, somewhat broad peak also is observed at 667 cm⁻¹, indicative of a Mo-O bond vibration where the oxygen is coordinated to three molybdenum atoms (ν OMo₃). Characteristic Raman shifts for α -MoO₃ also appear at lower wavenumbers and are associated with the A_g , B_{1g} , and B_{3g} bending modes (denoted $\partial OMo_{1, 2 \text{ or } 3}$).

In contrast, the Raman spectra acquired at Point B (Figure 3b), shows unique Raman shifts at 903, 850, 776, and 353 cm⁻¹ characteristic of monoclinic β -MoO₃. For the β -MoO₃ spectrum no peak is observed at 995 cm⁻¹ characteristic of the presence of the double bond Mo-O stretching vibration (molybdenum and a singly coordinated oxygen). The absence of this peak is also one of the clearest indications that a nonlayered phase exists within these regions. An exhaustive search of the literature reveals no spectral assignments to support the observed Raman peaks for β -MoO₃. However, since the structure of β -MoO₃ is crystallographically equivalent to that of WO₃, generalized structural assignments can be made on the basis of previously reported Raman spectral assignments for WO₃.^{4,5} In Table 1 we have grouped spectral assignments into modes that correspond to bond stretches and deformations. In accordance with the spectral interpretations made for WO₃, the Raman shifts located at 850 and 776 cm⁻¹ are attributed to Mo-O stretches, while the shifts at 418, 393, 353 and 313 cm⁻¹ are attributed to O-Mo-O deformations. Although, the small peak located at 903 cm⁻¹ cannot be assigned on the basis of a WO₃ crystal structure, this peak has been previously observed in β -MoO₃ by McCarron^{6,7,8} and by Kim.⁹ Since this stretch is found at high wavenumbers, it also most likely originates from a Mo-O stretch.

References.

- 1. Nakamoto, K. in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; p 147.
- 2. Nazri, G. A.; Julien, C. Solid State Ionics 1992, 53-56, 376.
- 3. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. in *Inorganic Chemistry*, 4th ed.; HarperCollins: New York, 1993; p A-15.
- 4. Mattes, R.; Schroder, F. Z. Naturforschg. 1969, 24b, 1095.
- 5. Anderson, A. Spectroscopy Lett. 1976, 9, 809.

- 6. McCarron III, E. M. J. Chem. Soc., Chem. Commun. 1986, 4, 336
- 7. Carcia, P. F.; McCarron III, E. M. Thin Solid Films 1987, 155, 53.
- 8. Parise, J. B.; McCarron III, E. M.; Von Dreele, R.; Goldstone, J. A. J. Solid State Chem. 1991, 93, 193.
- 9. Kim, H. -M.; Fukumoto, T.; Hayashi, S.; Yamamoto, K. J. Phys. Soc. Jpn. 1994, 63, 2194.