

Electronic Supplementary Information (ESI)

Discovering connections between Terahertz vibrations and elasticity underpinning the collective dynamics of the HKUST-1 metal-organic framework

Matthew R. Ryder,^{a,b} Bartolomeo Civalleri,^c Gianfelice Cinque^b and Jin-Chong Tan^{a,*}

^a Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK

^b Diamond Light Source, Harwell Campus, Didcot, Oxford OX11 0DE, UK

^c Department of Chemistry, NIS and INSTM Reference Centre, University of Turin,
via P. Giuria 7, 10125 Torino, Italy

*jin-chong.tan@eng.ox.ac.uk

Table of Contents

| | | |
|-----|---|---|
| 1 | HKUST-1 Lattice Parameters | 2 |
| 2 | Terahertz vibrational modes (< 600 cm ⁻¹) of HKUST-1 | 3 |
| 2.1 | IR active modes | 3 |
| 2.2 | Raman active modes | 4 |
| 2.3 | Non-optically active modes | 5 |
| 3 | Animations (movie clips) of THz collective lattice vibrations computed from <i>ab initio</i> density functional theory (DFT) | 7 |
| 3.1 | Low energy collective vibrations at 2.4 THz (81 cm ⁻¹) | 7 |
| 3.2 | Low energy collective vibrations at 1.7 THz (58 cm ⁻¹) | 7 |
| 3.3 | Low energy collective vibrations at 0.5 THz (16 cm ⁻¹) | 8 |
| 4 | Visualisation of all DFT calculated modes (0 – 3226 cm ⁻¹) | 9 |

1 HKUST-1 Lattice Parameters

| HKUST-1 (Fm-3m) | | |
|---|------------------------|--------------------------|
| Method | Lattice parameters (Å) | Volume (Å ³) |
| | a | |
| Experimental* | 26.304 | 691.90 |
| B3LYP | 26.327 | 693.11 |
| B3LYP-D | 26.296 | 691.48 |
| <ul style="list-style-type: none">• B3LYP error in lattice parameters: 0.09%• B3LYP-D error in lattice parameters: 0.03% | | |

* Local Vibrational Mechanism for Negative Thermal Expansion: A Combined Neutron Scattering and First-Principles Study

ANGEWANDTE CHEMIE INTERNATIONAL EDITION

Volume 49, Issue 3, January 12, 2010, Pages: 585–588, Vanessa K. Peterson,

Gordon J. Kearley, Yue Wu, Anibal Javier Ramirez-Cuesta, Ewout Kemner and Cameron J. Kepert

2 Terahertz vibrational modes (< 600 cm⁻¹) of HKUST-1

2.1 IR active modes

| Mode (cm ⁻¹) | IRREP | Description |
|--------------------------|-----------------|---|
| 81.47 | F _{1u} | Organic Linker Trampoline-like Motion |
| 138.88 | F _{1u} | Paddle Wheel Rocking with Organic Linker Rocking |
| 142.91 | F _{1u} | Paddle Wheel Deformation (Cu-Cu Buckling) and Translation with Linker Rocking |
| 192.76 | F _{1u} | Organic Linker Rocking |
| 250.10 | F _{1u} | Paddle Wheel Deformation (Strong Cu-Cu Buckling) |
| 288.99 | F _{1u} | Paddle Wheel Deformation (O-Cu-O Bending and Cu-Cu Buckling) |
| 294.17 | F _{1u} | Asymmetric Cu-O Stretching - Paddle Wheel Deformation (O-Cu-O Bending) |
| 303.05 | F _{1u} | |
| 344.19 | F _{1u} | Paddle Wheel Deformation with Linker Rocking |
| 500.18 | F _{1u} | OP Aromatic Ring Deformation |
| 527.83 | F _{1u} | IP Aromatic Ring Deformation with Partially Symmetric Cu-O Stretching |
| 550.42 | F _{1u} | Partially Symmetric Cu-O Stretching (Symmetric with respect to each carboxyl group) |

IRREP = Irreducible representation; IP = in-plane; OP = out-of-plane

2.2 Raman active modes

| Mode (cm⁻¹) | IRREP | Description |
|-----------------------------------|-----------------|---|
| 58.07 | F _{2g} | Strong Paddle Wheel Rotation with Organic Linker Trampoline-like Motion |
| 98.41 | A _g | Organic Linker Trampoline-like Motion (Symmetric Cluster Breathing) |
| 112.40 | E _g | Strong Paddle Wheel Deformation and Swelling/Breathing |
| 133.33 | F _{2g} | Asymmetric Paddle Wheel Deformation with Organic Linker Rocking |
| 138.93 | F _{2g} | |
| 150.91 | E _g | Paddle Wheel Rocking |
| 158.92 | F _{2g} | |
| 176.25 | E _g | Organic Linker Rocking |
| 198.81 | F _{2g} | |
| 214.35 | E _g | Paddle Wheel Swelling/Breathing (Cu-Cu Stretching) |
| 215.10 | A _g | |
| 263.44 | E _g | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending) |
| 269.24 | F _{2g} | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending and Cu-Cu Rocking) |
| 294.91 | E _g | Symmetric Cu-O Stretching - Paddle Wheel |
| 297.00 | F _{2g} | Swelling/Breathing (O-Cu-O Bending) with Linker Rocking |
| 303.36 | A _g | Symmetric Cu-O Stretching - Paddle Wheel |
| | | Swelling/Breathing (O-Cu-O Bending) |
| 316.02 | F _{2g} | Paddle Wheel Deformation with Linker Rocking |
| 322.83 | E _g | |
| 475.16 | F _{2g} | IP Aromatic Ring Deformation with Partially Symmetric Cu-O Stretching |
| 499.81 | F _{2g} | OP Aromatic Ring Deformation |
| 503.05 | E _g | |
| 519.49 | E _g | IP Aromatic Ring Deformation with Symmetric Cu-O Stretching |
| 524.80 | F _{2g} | |
| 537.82 | A _g | Symmetric Cu-O Stretching (Paddle Wheel Swelling/Breathing) |

IRREP = Irreducible representation; IP = in-plane; OP = out-of-plane

2.3 Non-optically active modes

| Mode (cm⁻¹) | IRREP | Description |
|-----------------------------------|-----------------|---|
| 16.32 | F _{2u} | Strong Paddle Wheel Deformation and Translational Motion (Symmetric Cluster Rotation) |
| 20.43 | E _u | Strong Paddle Wheel Deformation and Translational Motion |
| 63.17 | F _{2u} | Paddle Wheel Deformation and Translational Motion with Organic Linker Rotating |
| 78.28 | B _g | Paddle Wheel Deformation with Organic Linker Rotating (Symmetric Cluster Rocking) |
| 79.66 | A _u | Paddle Wheel Deformation with Organic Linker Rotating |
| 81.72 | F _{1g} | Paddle Wheel Deformation and Rotation with Organic Linker Rocking |
| 84.54 | F _{1g} | |
| 94.15 | B _u | Organic Linker Trampoline-like Motion |
| 102.09 | E _u | |
| 103.01 | F _{2u} | Strong Asymmetric Paddle Wheel Deformation and Rotation |
| 107.99 | A _u | |
| 118.29 | F _{1g} | |
| 137.97 | B _g | Paddle Wheel Rocking with Organic Linker Rocking (Symmetric Cluster Rocking) |
| 139.94 | F _{1g} | Paddle Wheel Rocking with Organic Linker Rocking |
| 141.64 | F _{2u} | |
| 160.95 | F _{1g} | Paddle Wheel Deformation |
| 170.78 | E _u | Organic Linker Rocking |
| 174.88 | B _u | Paddle Wheel Translational Motion |
| 191.10 | F _{2u} | Asymmetric Paddle Wheel Deformation (Cu-Cu Buckling) with Linker Rocking |
| 194.69 | E _u | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending) |
| 215.91 | F _{1g} | Paddle Wheel Rotation with Strong Linker Rocking |
| 239.39 | F _{2u} | Paddle Wheel Deformation (Strong Cu-Cu Buckling) with Linker Rocking |
| 262.09 | F _{1g} | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending) |
| 268.62 | B _g | |
| 270.22 | F _{1g} | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending and Cu-Cu Rocking) |
| 274.07 | F _{2u} | |
| 281.69 | E _u | Asymmetric Paddle Wheel Deformation (O-Cu-O Bending and Cu-Cu Buckling) |
| 298.14 | B _u | |
| 300.70 | F _{2u} | |

| | | |
|--------|----------|---|
| 303.88 | F_{1g} | Paddle Wheel Deformation with Linker Rocking |
| 317.89 | E_u | |
| 330.41 | F_{2u} | |
| 412.51 | A_u | |
| 441.34 | F_{2u} | IP Aromatic Ring Rotation with Asymmetric Cu-O Stretching |
| 456.51 | B_g | |
| 456.68 | F_{1g} | |
| 476.25 | F_{1g} | IP Aromatic Ring Deformation with Partially Symmetric Cu-O Stretching |
| 492.60 | F_{1g} | |
| 498.36 | F_{2u} | OP Aromatic Ring Deformation |
| 499.94 | E_u | |
| 519.46 | E_u | IP Aromatic Ring Deformation with Partially Symmetric Cu-O Stretching |
| 523.70 | F_{2u} | |
| 552.23 | B_u | Partially Symmetric Cu-O Stretching (Symmetric with respect to each carboxyl group) |
| 590.28 | E_u | Fully Asymmetric Cu-O Stretching (Asymmetric with respect to each carboxyl group) |

IRREP = Irreducible representation; IP = in-plane; OP = out-of-plane

3 Animations (movie clips) of THz collective lattice vibrations computed from *ab initio* density functional theory (DFT)

3.1 Low energy collective vibrations at 2.4 THz (81 cm⁻¹)

Views down the <111> and <110> directions, showing a ‘trampoline-like’ motion linked to negative thermal expansion (NTE).

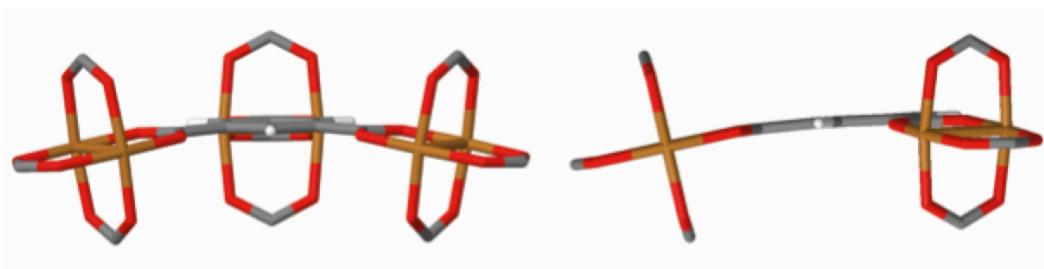
Movie clips URLs

<111> (Left panel):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_trampoline_81-47_111

<110> (Right panel):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_trampoline_81-47_110



3.2 Low energy collective vibrations at 1.7 THz (58 cm⁻¹)

Views down the <110> and <011> directions, showing a molecular rotor motion of the Cu-based paddle-wheel moiety.

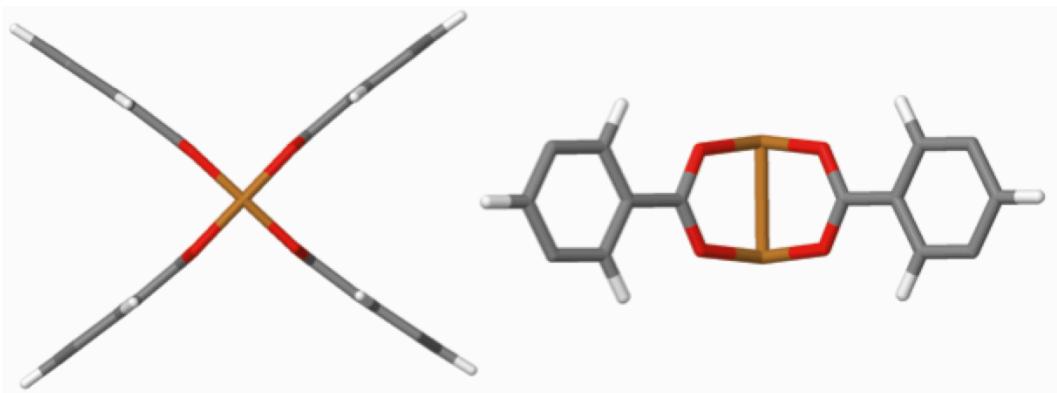
Movie clips URLs

<110> (Left):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_rotor_58-07_110

<011> (Right):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_rotor_58-07_011



3.3 Low energy collective vibrations at 0.5 THz (16 cm⁻¹)

Viewed down the <100> and <110> directions, showing a cluster rotation mechanism, which is potentially linked to auxeticity (negative Poisson's ratio).

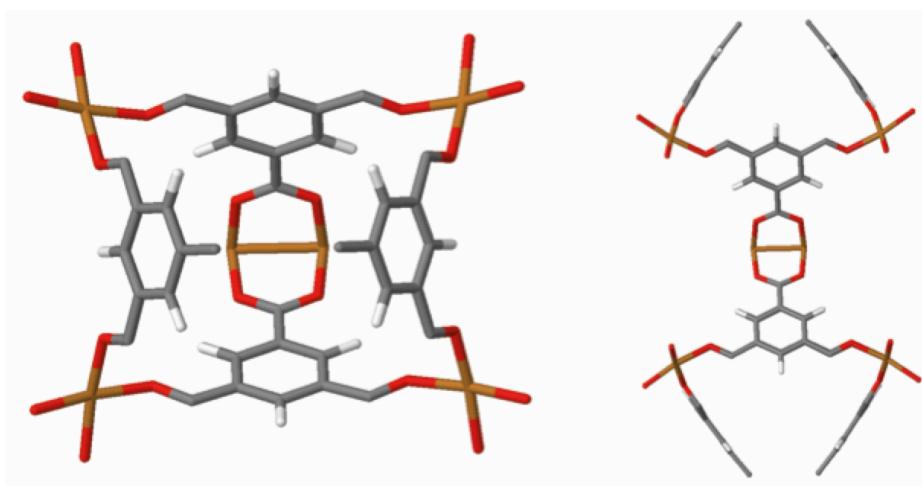
Movie clips URLs

<100> (Left):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_cluster_16-32_100

<110> (Right):

http://www.eng.ox.ac.uk/tan/thz-anim/hkust1_cluster_16-32_110



4 Visualisation of all DFT calculated modes (0 – 3226 cm⁻¹)

Link to animation hosted at University of Torino:
<http://www.crystal.unito.it/vibs/hkust%2D1/>

IMPORTANT: This animation requires latest version of Java to be unblocked and fully functional on the Firefox (Win/OSX) and Safari (OSX) browsers. It may not be compatible with other browsers.

