SUPPORTING INFORMATION

Infrared Signature of the Cation-π Interaction between Calcite and Aromatic Hydrocarbons

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Table S1. Impurities in Calcite

Element	Molar Percentage	Element	Molar Percentage
Sr	0.188494	Nb	0.000002
Y	0.000646	Eu	0.000002
Mo	0.000144	Cs	0.000002
La	0.000130	Tb	0.000001
Ni	0.000121	Tm	0.000001
Ce	0.000047	U	0.000001
Nd	0.000039	Sb	0.000001
Zr	0.000021	Lu	0.000001
Sn	0.000015	Bi	0.000000
V	0.000015	Cr	0.000000
Gd	0.000010	Co	0.000000
Dy	0.000010	Cu	0.000000
Pr	0.000009	Zn	0.000000
Li	0.000008	Ga	0.000000
Sm	0.000007	Rb	0.000000
Er	0.000007	Ba	0.000000
Yb	0.000004	Hf	0.000000
Be	0.000003	Ta	0.000000
Sc	0.000003	W	0.000000
Ho	0.000002	Th	0.000000
Pb	0.000002	**Sum**	0.189748

Table S2. Vibrational Modes of Benzene

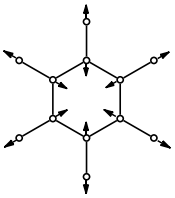
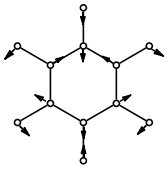
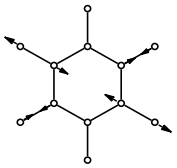
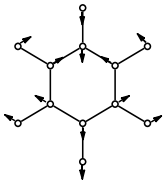
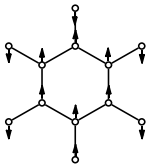
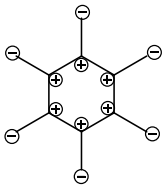
Aromatic C–H Stretch	 3091 cm^{-1}	 3071 cm^{-1}	 3036 cm^{-1}
Aromatic C–C Stretch	 1478 cm^{-1}		
Aromatic C–H In-Plane Bending	 1035 cm^{-1}		
Aromatic C–H Out-of-Plane Bending	 667 cm^{-1}		

Table S3. Vibrational Modes of Toluene

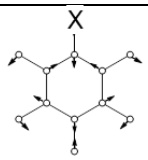
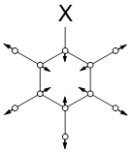
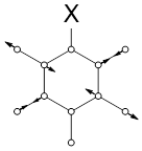
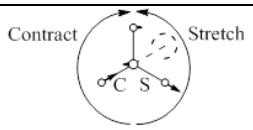
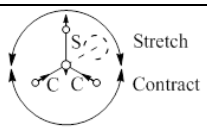
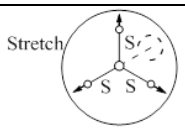
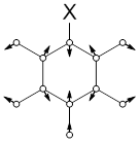
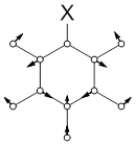
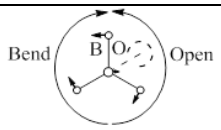
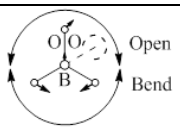
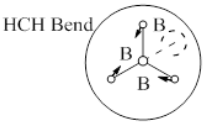
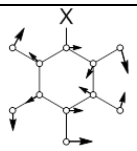
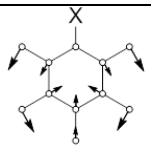
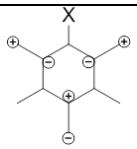
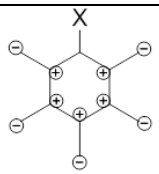
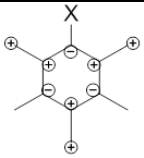
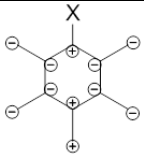
Aromatic C–H Stretch	 3087 cm^{-1}	 3062 cm^{-1}	 3026 cm^{-1}
Alkyl C–H Out-of-Phase Stretch	  2974 cm^{-1}		
Alkyl C–H In-Phase Stretch	 2872 cm^{-1}		
Quadrant Ring Stretch	 1605 cm^{-1}	 1496 cm^{-1}	
Alkyl C–H Out-of-Phase Deformation	  1459 cm^{-1}		Overtone (×2) 2919 cm^{-1}
Alkyl C–H In-Phase Deformation	 1379 cm^{-1}	Semi-Circle Ring Stretch	 1081 cm^{-1}
Aromatic C–H In-Plane Bending	 1030 cm^{-1}	Aromatic C–H Wag	 895 cm^{-1}
Aromatic C–H Out-of-Plane Bending	 726 cm^{-1}		
Ring Bending	 693 cm^{-1}	Out-of-Plane Quadrant Ring Bending	 463 cm^{-1}

Table S4. Vibrational Modes of Ethylbenzene

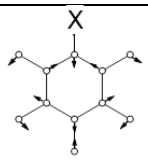
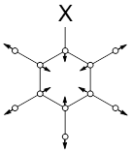
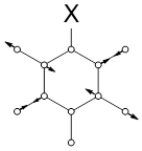
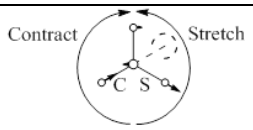
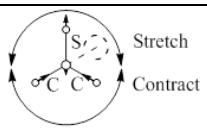
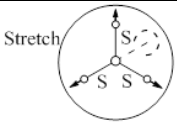
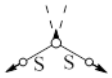
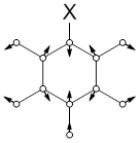
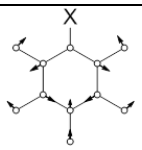
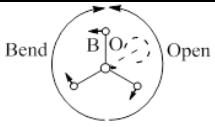
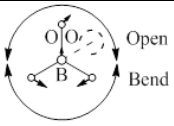
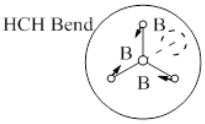
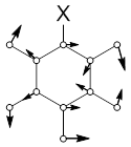
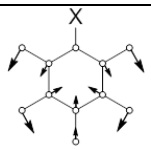
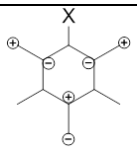
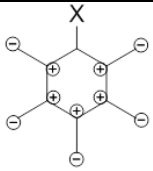
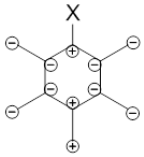
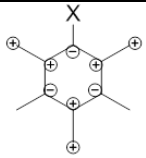
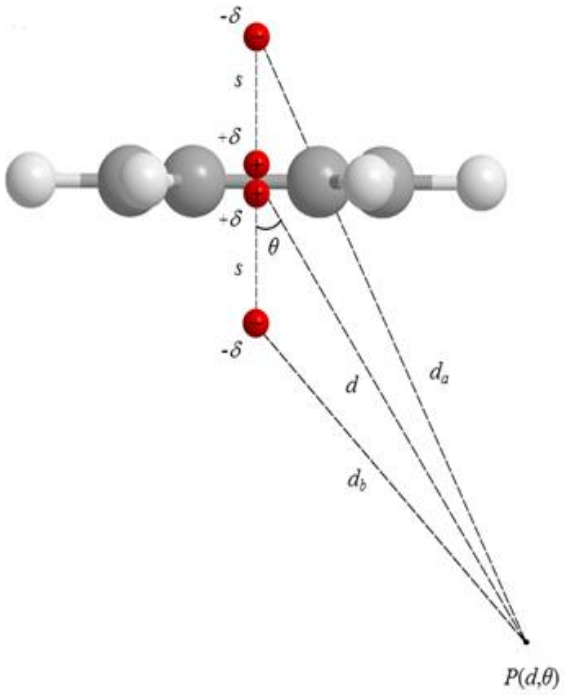
Aromatic C–H Stretch	 3086 cm^{-1}	 3064 cm^{-1}	 3027 cm^{-1}
Alkyl C–H Out-of-Phase Stretch	  2974 cm^{-1}	 2932 cm^{-1}	
Alkyl C–H In-Phase Stretch	 2896 cm^{-1}	 2874 cm^{-1}	
Quadrant Ring Stretch	 1604 cm^{-1}	 1496 cm^{-1}	
Alkyl C–H Out-of-Phase Deformation	  1453 cm^{-1}		
Alkyl C–H In-Phase Deformation	 1374 cm^{-1}	Semi-Circle Ring Stretch	 1090 cm^{-1}
Aromatic C–H In-Plane Bending	 1030 cm^{-1}	Aromatic C–H Wag	 904 cm^{-1}
Aromatic C–H Out-of-Plane Bending	 744 cm^{-1}	Out-of-Plane Quadrant Ring Bending	 555 cm^{-1}
Ring Bending	 696 cm^{-1}	485 cm^{-1}	

Table S5. Selected Geometry Parameters of Calcite-BTE Complexes

	$r_{C_{centroid}\text{-}Ca}$ (Å)	$r_{C_{ring}\text{-}Ca}$ (Å)	$r_{C_{ring}\text{-}C_{ring}}$ (Å)	$r_{C_{ring}\text{-}H}$ (Å)
benzene	3.35	3.03–4.14	1.40	1.09
toluene	3.43	3.08–4.21	1.40	1.09
ethylbenzene	3.40	3.10–4.19	1.40	1.09

Note S1. Estimation of the energy of cation-quadrupole interaction by classical electrostatics.

BTE molecule such as benzene has a linear quadrupole moment along the axis of rotational symmetry. The electric quadrupole moment can be approximated by two collinear pairs of point charges $-\delta$ and $+\delta$ separated by a distance s so that the moment $Q = -2\delta s^2$.



The potential at an arbitrary point $P(d,\theta)$ is given by the superposition of the potentials due to each point charge:

$$V(d,\theta) = \frac{\delta}{4\pi\varepsilon_0}\left(\frac{1}{d_a}+\frac{1}{d_b}-\frac{2}{d}\right) = \frac{\delta}{4\pi\varepsilon_0 d}\left(\frac{d}{d_a}+\frac{d}{d_b}-2\right) \qquad \text{(S1)}$$

where the permittivity of free space ε_0 = 8.85×10^{-12} C^2 J^{-1} m^{-1} and d_a and d_b are the distances from point P to the top and bottom of the quadrupole. Since

$$d_a^2 = d^2 + s^2 - 2ds\cos(\pi-\theta) = d^2 + s^2 + 2ds\cos\theta \qquad \text{(S2)}$$

So

$$\frac{d_a}{d} = \sqrt{1+\left(\frac{s}{d}\right)^2 + 2\frac{s}{d}\cos\theta} \qquad \text{(S3)}$$

For $\left(\frac{s}{d}\right)^2 + 2\frac{s}{d}\cos\theta \to 0$, an approximation is obtained from the first three terms of the Taylor series:

$$\frac{d}{d_a} = 1 - \frac{s}{d}\cos\theta + \left(\frac{s}{d}\right)^2 \frac{3\cos^2\theta - 1}{2} \qquad \text{(S4)}$$

Similarly,

$$\frac{d}{d_b} = 1 + \frac{s}{d}\cos\theta + \left(\frac{s}{d}\right)^2 \frac{3\cos^2\theta - 1}{2} \qquad \text{(S5)}$$

Combining Eq. S1, S4, and S5 gives:

$$V(d,\theta) = \frac{\delta s^2}{4\pi\varepsilon_0 d^3}\left(3\cos^2\theta - 1\right) = \frac{-Q}{8\pi\varepsilon_0 d^3}\left(3\cos^2\theta - 1\right) \qquad \text{(S6)}$$

So the interaction energy between one mole of the BTE quadrupole and the calcium cation is:

$$E(d,\theta) = \frac{-qQN}{8\pi\varepsilon_0 d^3}\left(3\cos^2\theta - 1\right) \qquad \text{(S7)}$$

where q is the charge of the calcium cation and N is the Avogadro's number, 6.02×10^{23}. Each calcium cation possesses two positive elementary charges and has six bonds in calcite and the cleavage at the $(10\bar{1}4)$ surface breaks one of them, so

$$q = \frac{2e}{6} \qquad \text{(S8)}$$

where the elementary charge $e = 1.6\times10^{-19}$ C. Combining Eq. S7 and S8 gives the interaction energy for one mole of BTE molecules to be:

$$E(d,\theta) = \frac{-eQN}{24\pi\varepsilon_0 d^3}\left(3\cos^2\theta - 1\right) \qquad \text{(S9)}$$

Replacing the constants with numerical values and recognizing $d = r_{C_{centroid}\text{-}Ca}$, we have

$$E(d,\theta) = -\frac{48Q}{d^3}\left(3\cos^2\theta - 1\right) \qquad \text{(S10)}$$

where Q has a unit of Buckingham (1 Buckingham = 1 Debye Å = 3.34×10^{-40} C m), $r_{C_{centroid}\text{-}Ca}$ has a unit of Å, and E has a unit of kJ mol^{-1}.