SUPPORTING INFORMATION

Raman spectra of Titanium Dioxide (Anatase, Rutile) with Identified Oxygen Isotopes (16, 17, 18)

Otakar Frank[a], Marketa Zukalova[a], Barbora Laskova[a], Jenő Kürti[b], János Koltai[b] and Ladislav Kavan[a]

[a] *J. Heyrovský Institute of Physical Chemistry, v.v.i. Academy of Sciences of the Czech Republic, Dolejskova 3, 18223 Prague 8, Czech Republic*

[b] *Institute of Physics, Loránd Eötvös University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary*

Table S1. Full widths at half-maxima of the $Ti^{16}O_2$, $Ti^{17}O_2$, and $Ti^{18}O_2$ rutile bands, obtained experimentally at 295 K and 5 K (Lorentzian shapes).

Mode	FWHM @ 295K (cm^{-1})			FWHM @ 5K (cm^{-1})		
	$Ti^{16}O_2$	$Ti^{17}O_2$	$Ti^{18}O_2$	$Ti^{16}O_2$	$Ti^{17}O_2$	$Ti^{18}O_2$
B_{1g}	2.5	7.2	5.5	1.2	2.1	2
E_g	40.5	40.4	37.1	11.3	20.8	10.2
A_{1g}	41.9	45.9	41.7	23.5	27.1	20.5
B_{2g}	11	38.1	12.9	---	---	---

Table S2. List of possible combination modes in $Ti^{16}O_2$ and $Ti^{18}O_2$ rutile with the Raman shifts (ν_{16}, ν_{18}) calculated from LDA and from experimental values. In the latter case, Raman shift values of B_{1g}, E_g, A_{1g} modes acquired at 5 K (see Table 1, main text) were utilized to calculate the frequency of the particular combination mode (where possible). In the right columns ("Measured 5 K"), is the list of combination modes fitted to the experimental spectra. It is given at positions approximately corresponding to the calculated frequencies. The u⊕g combinations are omitted and the $A_1 \otimes A_2$ and $B_1 \otimes B_2$ combinations are marked with dark background (see the main text for discussion).

Combination	**Calculated LDA (cm^{-1})**			**Calculated from exp. 5 K (cm^{-1})**			**Measured 5 K (cm^{-1})**		
	ν_{16}	ν_{18}	Δ_{1618}	ν_{16}	ν_{18}	Δ_{1618}	ν_{16}	ν_{18}	Δ_{1618}
$E_u(1)$ - A_{2u}	3.3	3.5	-0.2						
$B_{1u}(2)$ - $E_u(2)$	15.7	4.3	11.4						
A_{2u} - $B_{1u}(1)$	45.2	39.9	5.3						
E_g - A_{2g}	47.1	44.4	2.7						
$E_u(1)$ - $B_{1u}(1)$	48.5	43.4	5.1						
$E_u(3)$ - $B_{1u}(2)$	89.7	97.6	-7.9						
$E_u(3)$ - $E_u(2)$	105.5	101.9	3.5						
A_{1g} - E_g	148.3	139.8	8.5	156.4	148.6	7.8	157.2	---	---
$B_{1u}(1)$ + $B_{1u}(1)$	187.1	187.0	0.1				165.4	161.5	3.9
A_{1g} - A_{2g}	195.4	184.2	11.2				181.5	174.0	-1.3
B_{2g} - A_{1g}	204.6	192.9	11.7				195.5	193.0	2.5
$B_{1u}(1)$ + A_{2u}	232.3	226.9	5.4				215.5	213.5	2.0
$B_{1u}(1)$ + $E_u(1)$	235.6	230.4	5.2				236.5	236.3	0.2
$E_u(2)$ - $E_u(1)$	242.6	236.6	6.0				250.3	250.6	-0.3
$E_u(2)$ - A_{2u}	245.9	240.1	5.8				264.4	264.7	-0.3
$B_{1u}(2)$ - $E_u(1)$	258.4	240.9	17.5						
$B_{1u}(2)$ - A_{2u}	261.6	244.4	17.3						
A_{2u} + A_{2u}	277.5	266.8	10.7						
A_{2g} - B_{1g}	278.0	262.1	15.9						
A_{2u} + $E_u(1)$	280.8	270.3	10.5				---	286.7	---
B_{1g} + B_{1g}	282.4	266.2	16.1	285.4	266.4	19.0			
$E_u(1)$ + $E_u(1)$	284.1	273.8	10.3				303.7	295.9	10.6
$E_u(2)$ - $B_{1u}(1)$	291.1	280.0	11.1						
$B_{1u}(2)$ - $B_{1u}(1)$	306.8	284.3	22.6						
E_g - B_{1g}	325.1	306.5	18.6	310.7	297.3	13.4	319.9	306.4	13.5
$E_u(3)$ - $E_u(1)$	348.1	338.5	9.6				340.1	328.1	12.0
$E_u(3)$ - A_{2u}	351.4	342.0	9.4				354.4	343.8	10.6
B_{2g} - E_g	352.9	332.7	20.2						
$E_u(3)$ - $B_{1u}(1)$	396.6	381.9	14.7				372.9	359.3	13.6
B_{2g} - A_{2g}	400.0	377.1	22.9				405.2	384.6	20.6
A_{1g} - B_{1g}	473.3	446.3	27.1	467.1	445.9	21.2			
$B_{1u}(1)$ + $E_u(2)$	478.2	467.0	11.3						
$B_{1u}(1)$ + $B_{1u}(2)$	494.0	471.3	22.7						
A_{2u} + $E_u(2)$	523.4	506.9	16.5				508.3	491.6	16.7
$E_u(1)$ + $E_u(2)$	526.7	510.4	16.3						
A_{2u} + $B_{1u}(2)$	539.2	511.2	28.0						
$E_u(1)$ + $B_{1u}(2)$	542.5	514.7	27.8						
B_{1g} + A_{2g}	560.3	528.3	32.0						
$B_{1u}(1)$ + $E_u(3)$	583.7	568.9	14.8						
B_{1g} + E_g	607.5	572.7	34.7	596.1	563.7	32.4			
A_{2u} + $E_u(3)$	628.9	608.8	20.1						
$E_u(1)$ + $E_u(3)$	632.2	612.3	19.9						
B_{2g} - B_{1g}	678.0	639.2	38.8				691.7	660.2	31.5
B_{1g} + A_{1g}	755.7	712.5	43.2	752.5	712.3	40.2			

$E_u(2) + E_u(2)$	769.3	746.9	22.4			
$E_u(2) + B_{1u}(2)$	785.1	751.2	33.8			
$B_{1u}(2) + B_{1u}(2)$	800.8	755.6	45.3			
$A_{2g} + A_{2g}$	838.3	790.4	47.9			
$E_u(2) + E_u(3)$	874.8	848.9	25.9			
$A_{2g} + E_g$	885.4	834.8	50.6			
$B_{1u}(2) + E_u(3)$	890.6	853.2	37.4			
$E_g + E_g$	932.6	879.2	53.3	906.8	861.0	45.8
$B_{1g} + B_{2g}$	960.3	905.4	54.9			
$E_u(3) + E_u(3)$	980.3	950.8	29.5			
$A_{2g} + A_{1g}$	1033.7	974.6	59.1			
$E_g + A_{1g}$	1080.8	1019.0	61.8	1063.2	1009.6	53.6
$A_{1g} + A_{1g}$	1229.0	1158.8	70.3	1219.6	1158.2	61.4
$A_{2g} + B_{2g}$	1238.3	1167.5	70.8			
$E_g + B_{2g}$	1285.4	1211.9	73.5			
$A_{1g} + B_{2g}$	1433.7	1351.7	82.0			
$B_{2g} + B_{2g}$	1638.3	1544.6	93.7			

Table S3. Full widths at half-maxima of the $Ti^{16}O_2$, $Ti^{17}O_2$, and $Ti^{18}O_2$ anatase bands, obtained experimentally at 295 K and 5 K (Lorentzian shapes). The $E_g(2)$ mode is omitted due to high uncertainty in the fitting procedure.

Mode	FWHM @ 295K (cm^{-1})			FWHM @ 5K (cm^{-1})		
	$Ti^{16}O_2$	$Ti^{17}O_2$	$Ti^{18}O_2$	$Ti^{16}O_2$	$Ti^{17}O_2$	$Ti^{18}O_2$
$E_g(1)$	13.3	15.5	12.8	4.8	9.4	4.5
$B_{1g}(1)$	32.3	35.6	24.8	9.6	17.6	8.1
$B_{1g}(2)$	32.0	39.4	29.3	3.7	6.4	3.0
A_{1g}				13.6	17.1	14.8
$E_g(3)$	31.4	32.9	25.4	13.9	19.3	14.0

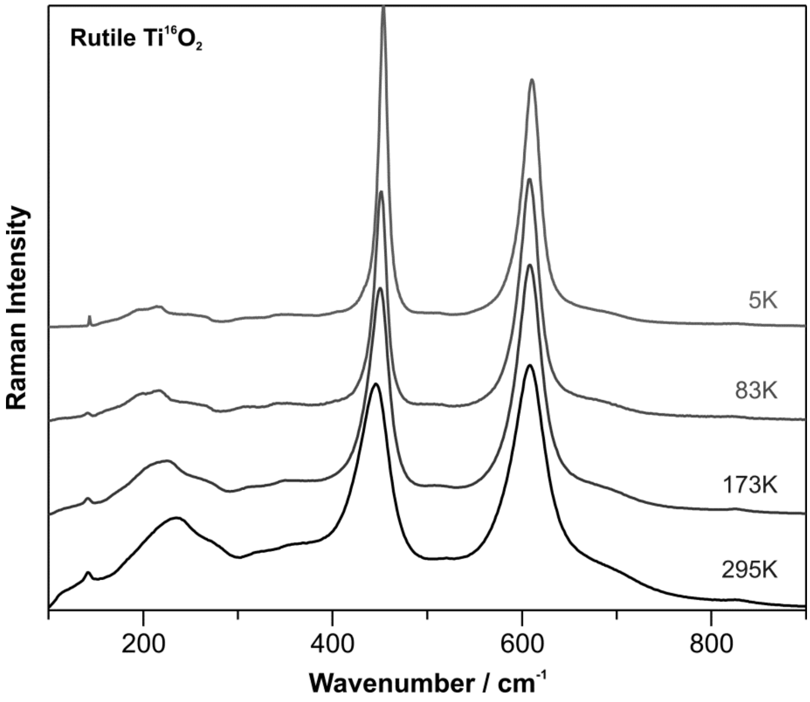

Figure S1. Evolution of the Raman spectra of Ti^{16}O$_2$ rutile with temperature

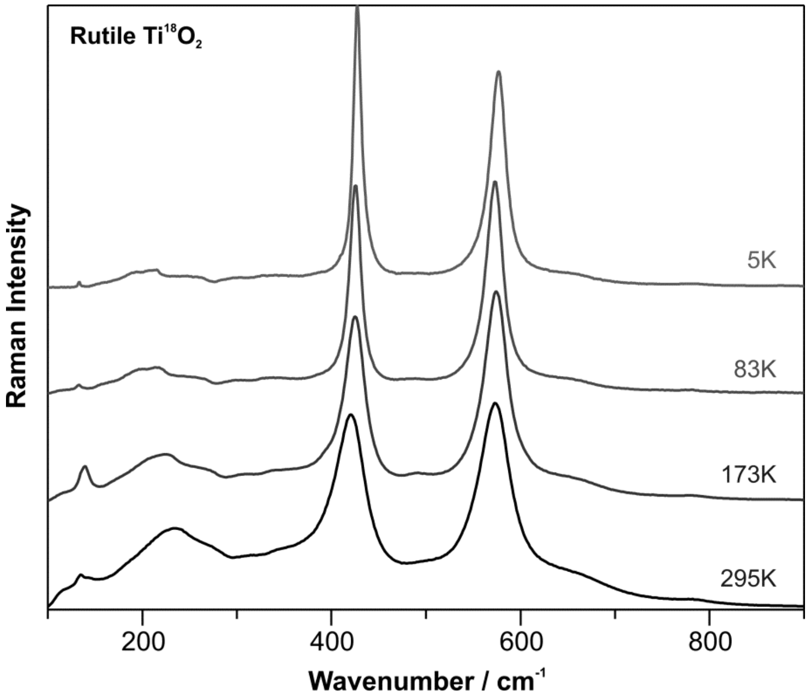

Figure S2. Evolution of the Raman spectra of Ti^{18}O$_2$ rutile with temperature.

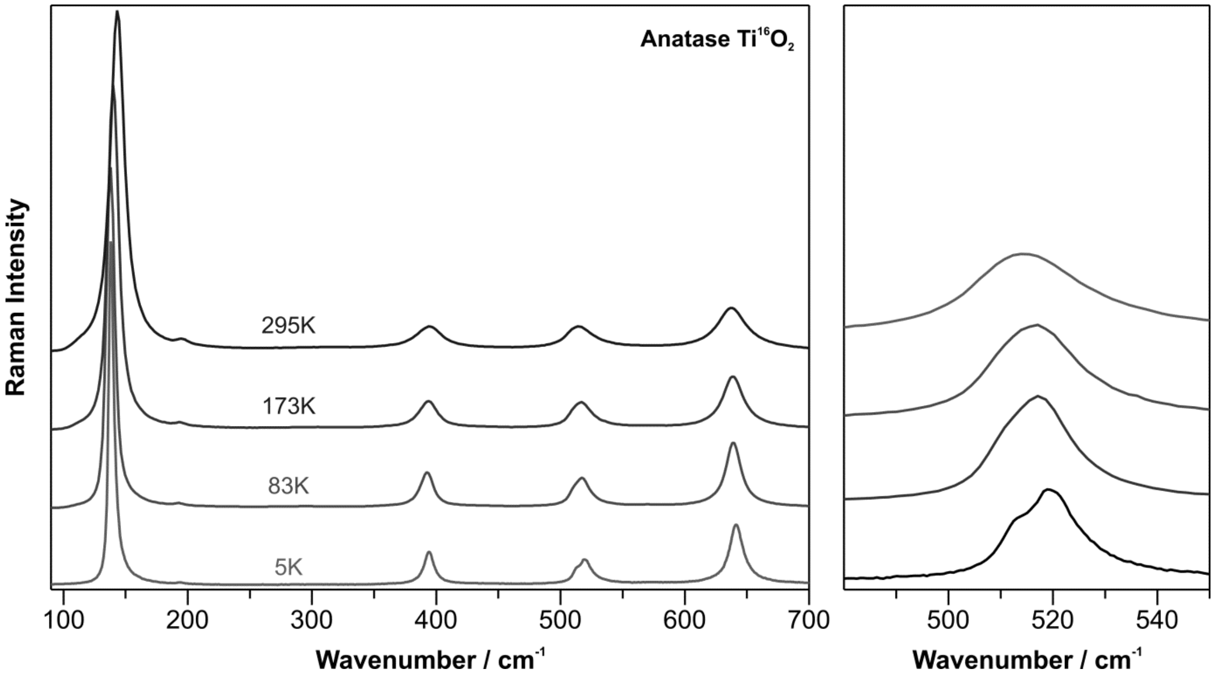

Figure S3. Evolution of the Raman spectra of Ti^{16}O$_2$ anatase with temperature with a magnified view of the $B_{1g}(2)$ and A_{1g} mode region (right). The spectra are normalized on the $E_g(1)$ mode amplitude.

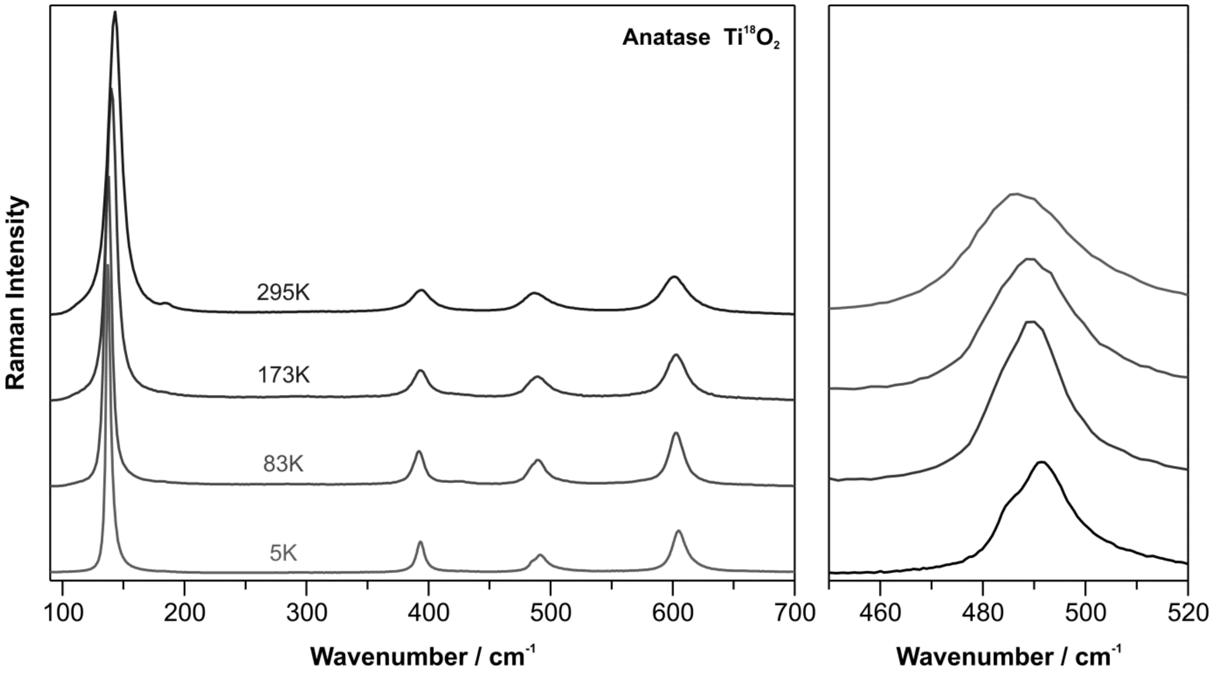

Figure S4. Evolution of the Raman spectra of Ti^{18}O$_2$ anatase with temperature with a magnified view of the $B_{1g}(2)$ and A_{1g} mode region (right). The spectra are normalized on the $E_g(1)$ mode amplitude.