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# **Resolving the strange behaviour of extra-terrestrial potassium in the upper atmosphere**

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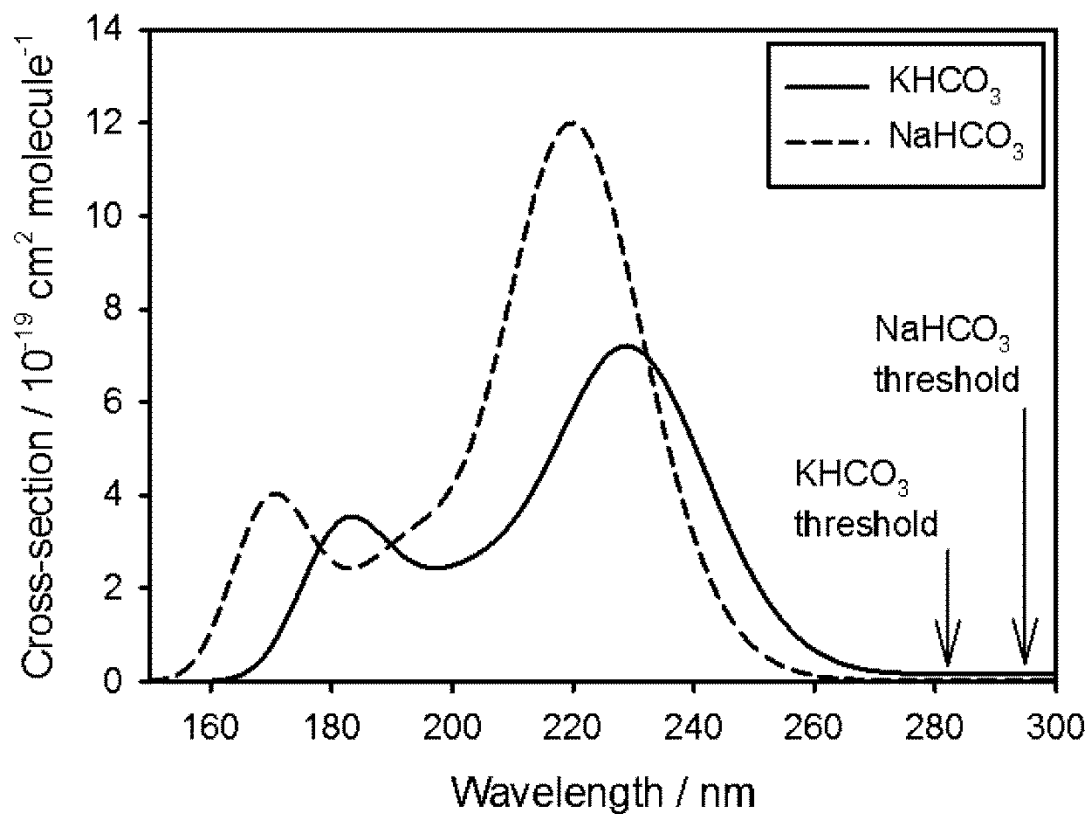
**Supplementary Material for MS# 2014GL060334**

**Table S1.** Calculated molecular parameters at the B3LYP/6-311+G(2d,p) level of theory

Molecule	Geometry <sup>a</sup>	Rotational constants <sup>b</sup>	Vibrational frequencies <sup>c</sup>
KOH	K, 0.,0.,0.005 O, 0.,0.,2.21 H, 0.,0.,3.17	8.186	347, 347, 447, 3914
K(OH)CO <sub>2</sub>	K, 1.922, 0.168,0.074 O, -0.255,-1.150,0.021 O, -0.343,1.099,0.0369 O, -2.278,-0.0973,-0.010 C, -1.077,0.086,0.015 H, 0,-0.899,-1.868,0.002	11.459, 2.076, 1.758	68, 186, 257, 520, 544, 602, 796, 804, 1164, 1283, 1825, 3823
K(OH)CO <sub>2</sub> → KHCO <sub>3</sub> transition state via H transfer	K, 2.025,-0.294,-0.034 O, -0.378,-1.051,-0.020 O, 0.012,1.213,0.022 O, -2.063,0.201,0.026 C, -0.771,0.257,0.011 H, -1.627,-1.020,-0.004	11.445, 2.156, 1.814	1848i, 78, 195, 246, 628, 754, 809, 1043, 1112, 1355,1667, 2247
K(OH)CO <sub>2</sub> → KHCO <sub>3</sub> transition state via K transfer	K, -0.041,-0.000,0.058 O, -0.005,0.000,4.105 O, 0.976,0.000,2.115 O, 2.247,-0.001,3.981 C, 1.1889,-0.000,3.366 H, 0.283,-0.000,5.027	12.033, 1.483, 1.320	-36i, 270, 567, 576, 650 824, 951, 1225, 1345, 1751, 3802
KHCO <sub>3</sub>	K, 2.190,-0.0403,-0.0 O, -0.088,-1.106,-0.0 O, -0.021,1.142,-0.0 O, -1.989,0.0945,0.0 C, -0.617,0.043,0.0 H, -2.279,-0.827,0.0	12.241, 2.085, 1.782	78, 195, 254, 570, 579, 684, 834, 995, 1235, 1373, 1669 3803
KHCO <sub>3</sub> + H → K + H <sub>2</sub> CO <sub>3</sub> transition state	K, 0.004,-0.013,-0.025 O,-0.003,-0.003,2.740 O, 1.958,0.011,1.621 O, 1.954,-0.125,3.846 C, 1.303,-0.017,2.662 H, 1.275,-0.170,4.532 H, -0.556,-1.060,2.188	11.296, 1.894, 1.634	1130i, 60, 92, 214, 502, 558, 570, 647, 688, 837, 1002,1217, 1356, 1694, 3796

<sup>a</sup> Cartesian co-ordinates; <sup>b</sup> GHz; <sup>c</sup> cm<sup>-1</sup>

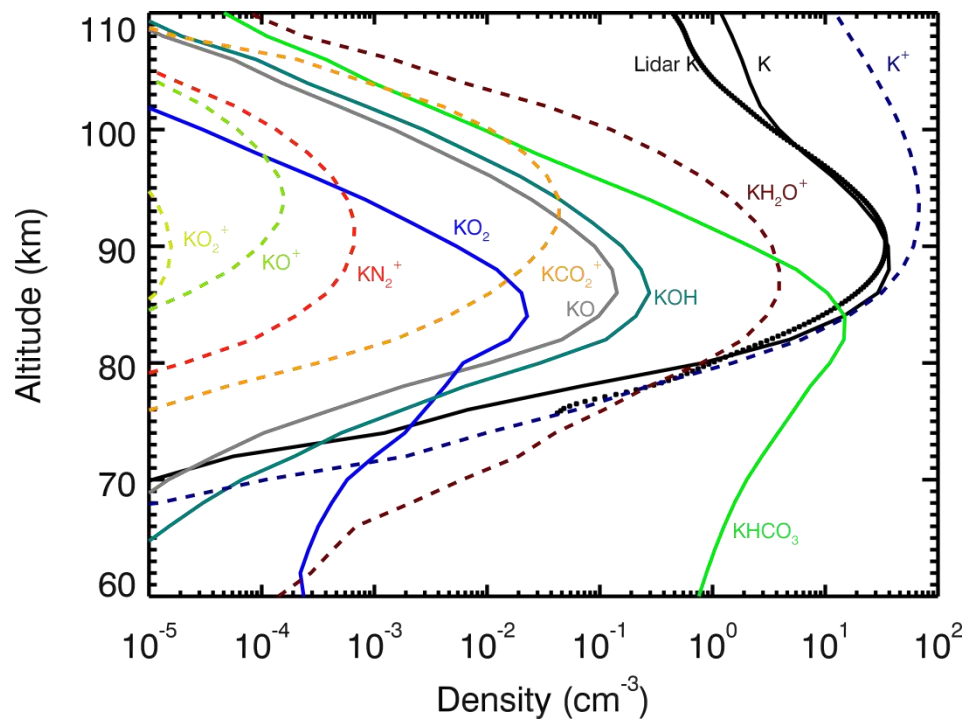
Figure S1.



Theoretical photodissociation cross sections of  $\text{KHCO}_3$  and  $\text{NaHCO}_3$ , calculated at the TD/B3LYP/6-311+g(2d,p) level of theory and placed on an absolute scale using the measured  $\text{NaHCO}_3$  cross section [Self and Plane, 2002].

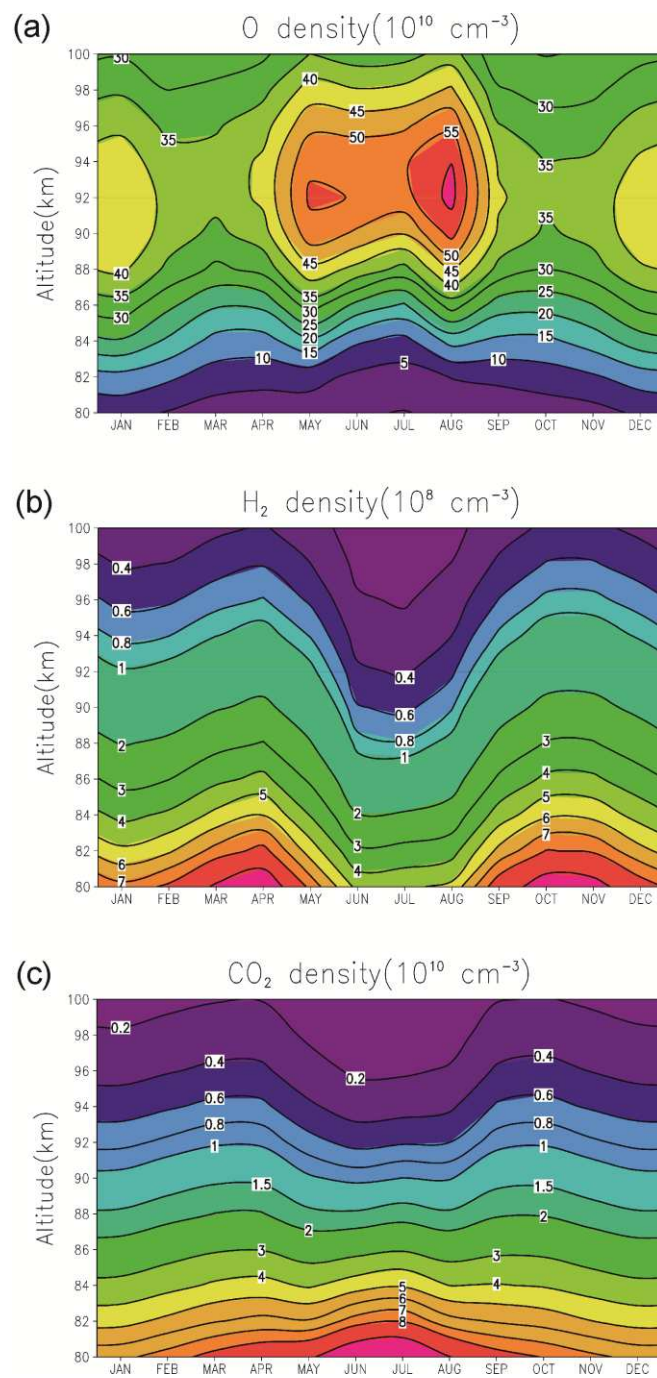
Self, D. E., and J. M. C. Plane (2002), Absolute photolysis cross-sections for  $\text{NaHCO}_3$ ,  $\text{NaOH}$ ,  $\text{NaO}$ ,  $\text{NaO}_2$  and  $\text{NaO}_3$ : implications for sodium chemistry in the upper mesosphere, *Phys. Chem. Chem. Phys.*, 4(1), 16-23.

Figure S2.



Concentration profiles of the K-containing species in WACCM-K, averaged from 2004-2006 at 54°N. The average K layer during this period, measured by resonance lidar at Kühlungsborn, Germany, is shown with black diamonds.

**Figure S3.**



Seasonal variation of the density profiles of (a) atomic O, (b) H<sub>2</sub> and (c) CO<sub>2</sub> at 54° N, averaged from 2004-2006 in the WACCM-K model.