Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Isotopic separation of helium through graphyne membranes: a ring polymer molecular dynamics study (Electronic Supplementary Information)

Somnath Bhowmick,[a,b,*] Marta I. Hernández,[c] José Campos-Martínez,[c,*] Yury V. Suleimanov[a,*]

[a] *Computation-based Science and Technology Research Center, The Cyprus Institute, 20 Konstantinou Kavafi Street, Nicosia 2121, Cyprus*
[b] *Climate & Atmosphere Research Centre, The Cyprus Institute, 20 Konstantinou Kavafi Street, Nicosia 2121, Cyprus*
[c] *Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain*

Email: *s.bhowmick@cyi.ac.cy*, *j.campos.martinez@csic.es*, *y.suleymanov@cyi.ac.cy*

1. Potential of mean force

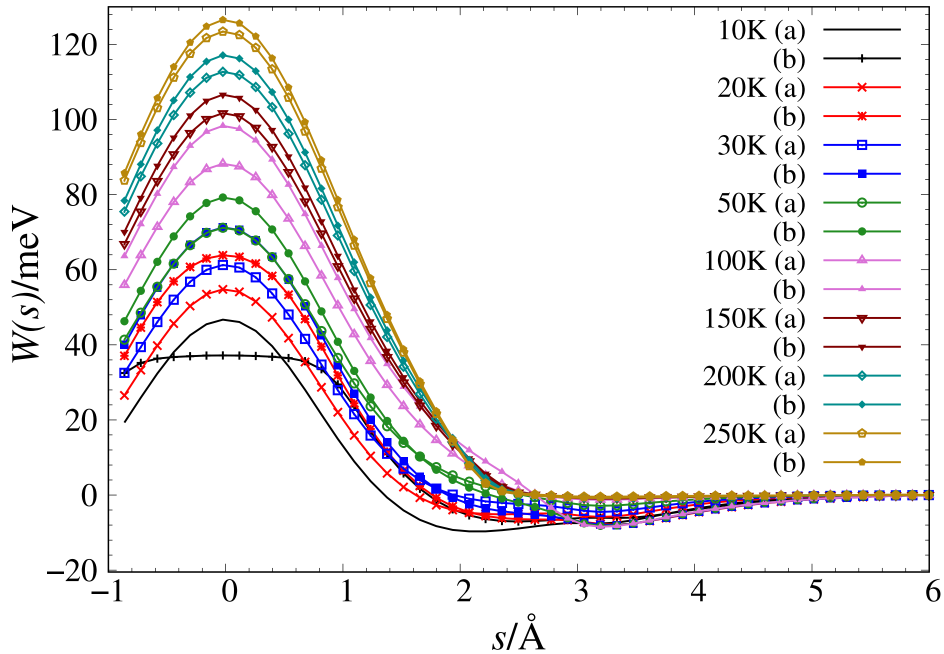

Fig. S1: Variation of the (a) classical and (b) RPMD potential of mean force, $W(s)$, (in meV) for ^{3}He atom along the reaction coordinate s (in Å) perpendicular to the graphdiyne membrane within the temperature range 10−250 K.

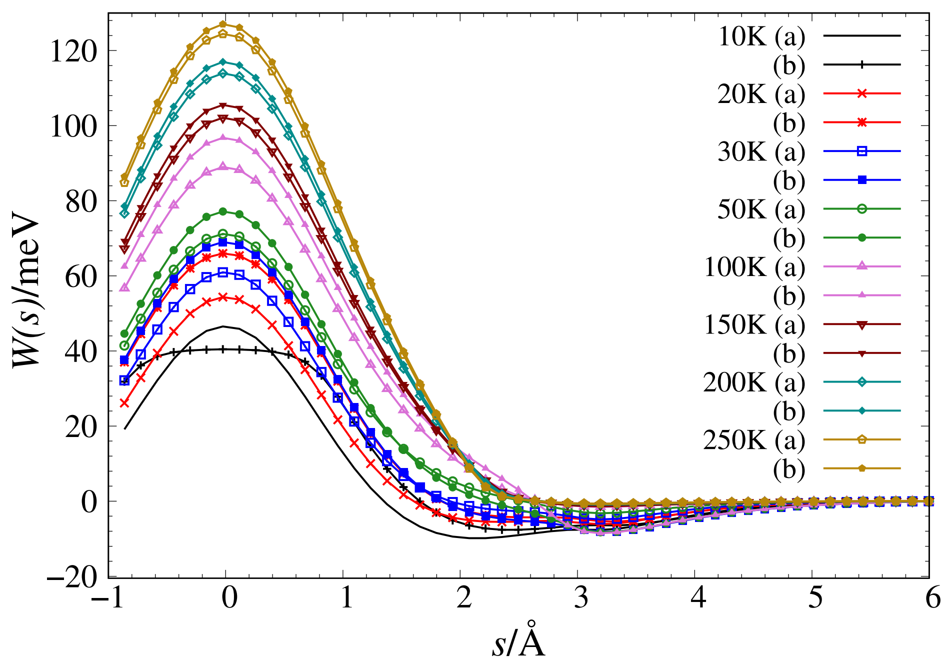

Fig. S2: Variation of the (a) classical and (b) RPMD potential of mean force, $W(s)$, (in meV) for ^{4}He atom along the reaction coordinate s (in Å) perpendicular to the graphdiyne membrane within the temperature range 10−250 K.

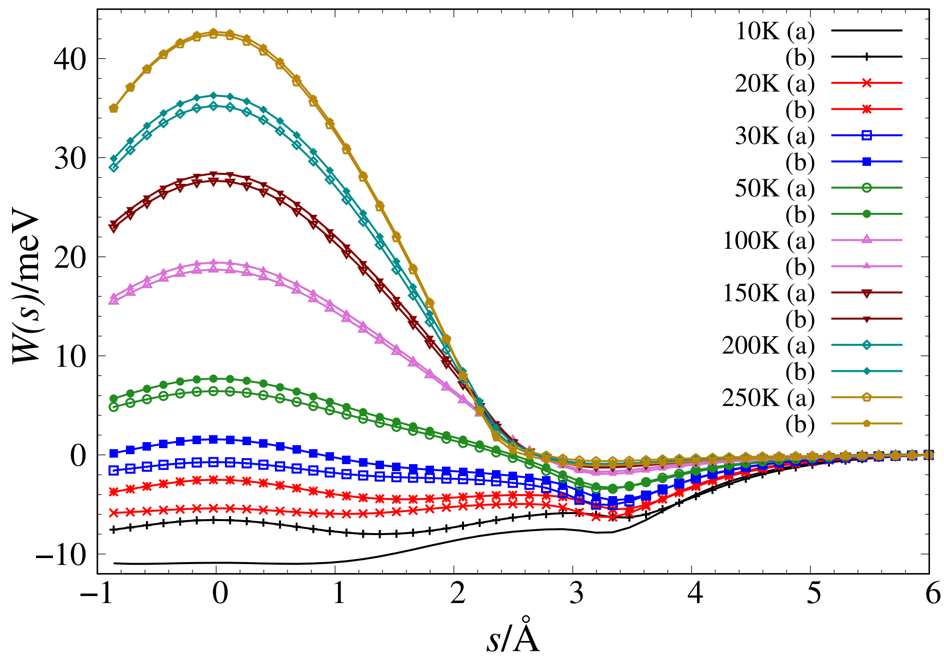

Fig. S3: Variation of the (a) classical and (b) RPMD potential of mean force, $W(s)$, (in meV) for ^{3}He atom along the reaction coordinate s (in Å) perpendicular to the graphtriyne membrane within the temperature range 10−250 K.

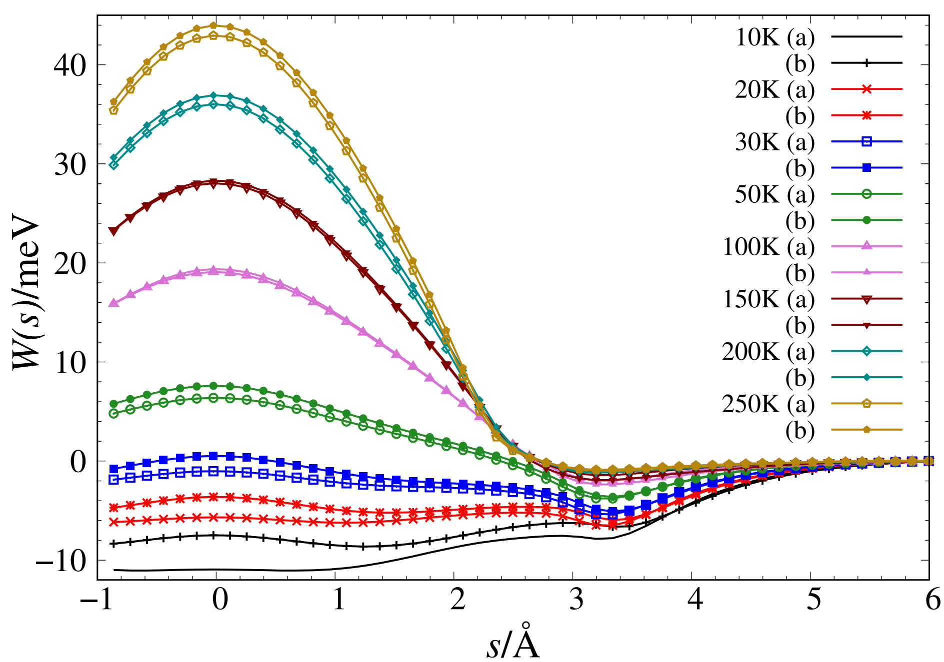

Fig. S4: Variation of the (a) classical and (b) RPMD potential of mean force, $W(s)$, (in meV) for ^{4}He atom along the reaction coordinate s (in Å) perpendicular to the graphtriyne membrane within the temperature range 10−250 K.

2. Ring polymer transmission coefficient

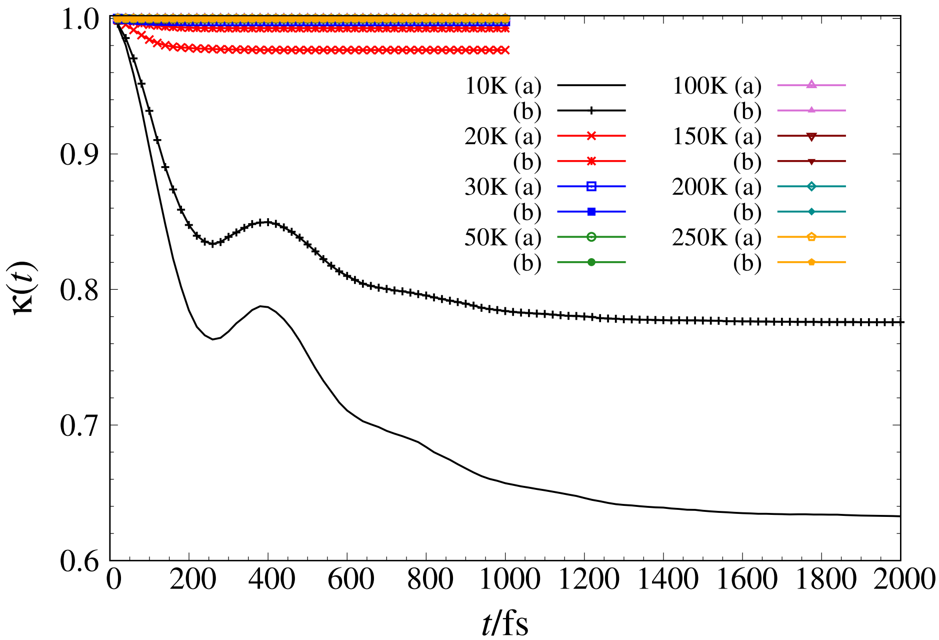

Fig. S5: Ring polymer time dependent transmission coefficient, $\kappa(t)$, in the temperature range 10−250 K for (a) ^{3}He and (b) ^{4}He atom transmission through the graphdiyne membrane.

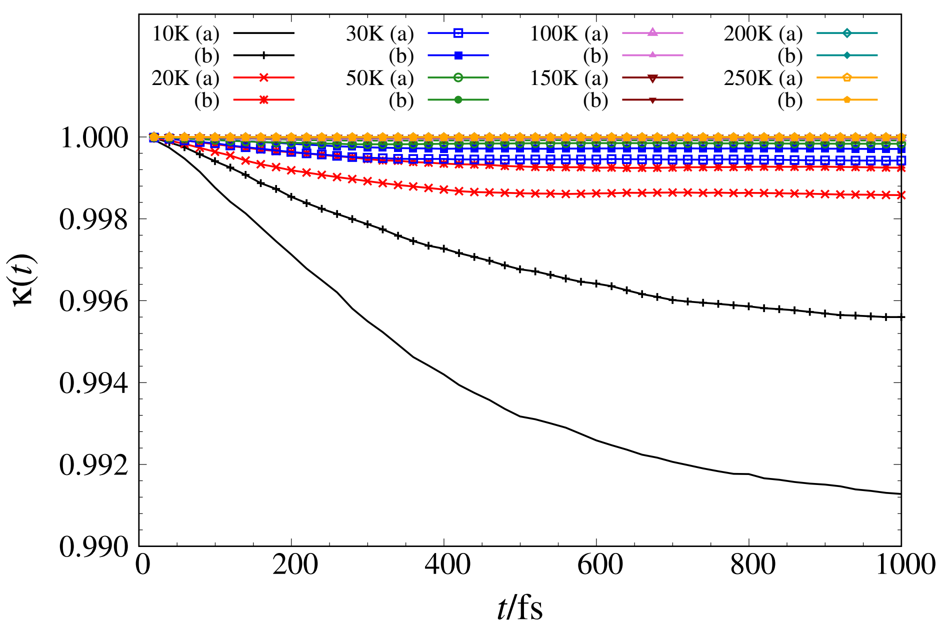

Fig. S6: Ring polymer time dependent transmission coefficient, $\kappa(t)$, in the temperature range 10−250 K for (a) ^{3}He and (b) ^{4}He atom transmission through the graphtriyne membrane.

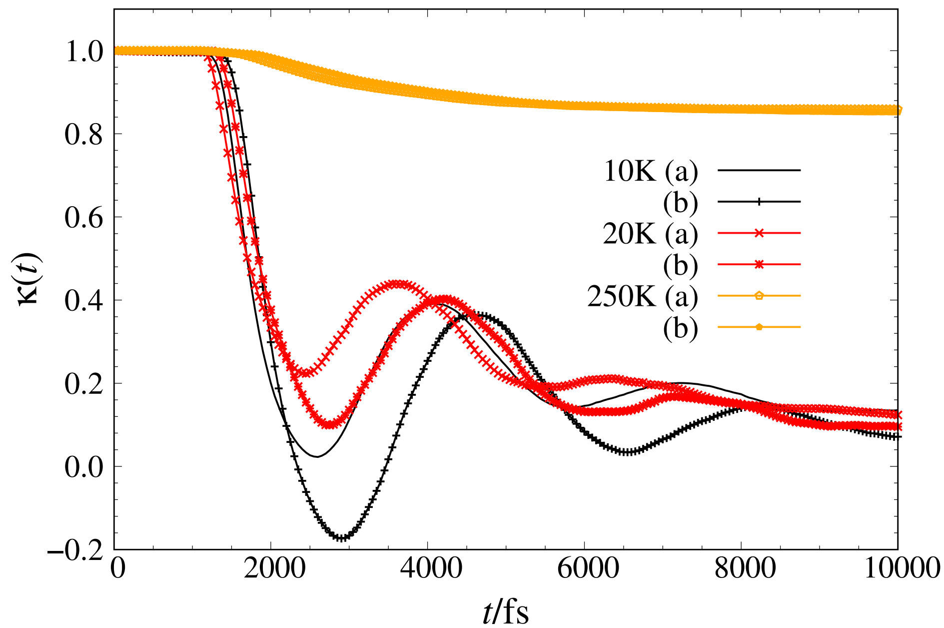

Fig. S7: Ring polymer time dependent transmission coefficient, $\kappa(t)$, at temperatures 10 K, 20 K, and 250 K for (a) ^{3}He and (b) ^{4}He atom transmission through the graphtriyne membrane.

3. Rate coefficient and selectivity

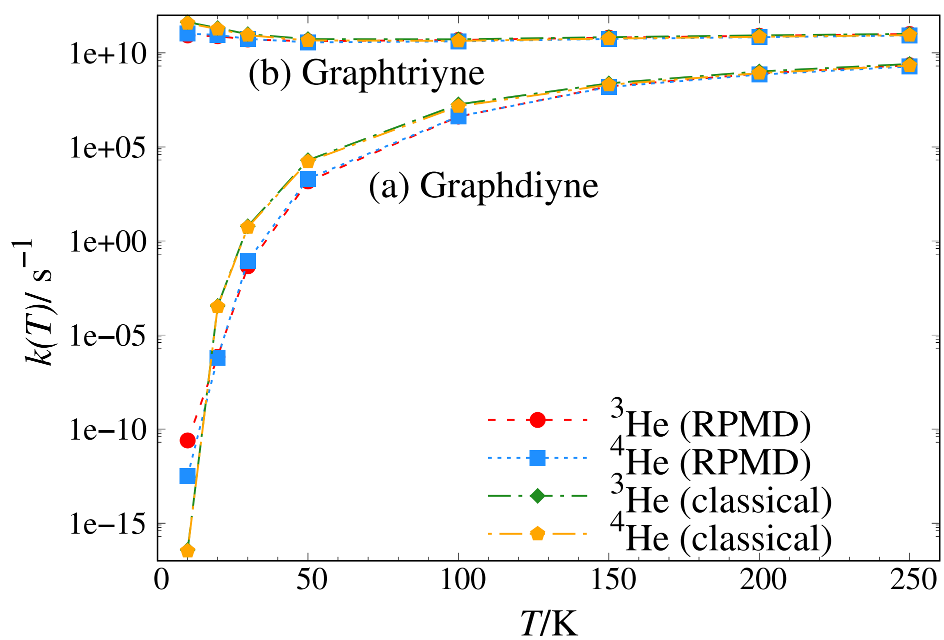

Fig. S8: Variation of the ring polymer molecular dynamics, RPMD (k_{RPMD}) and classical (k_{cl}) rate coefficients (in s^{-1}) for the transmission of ^{3}He [red circle (RPMD) and green diamond (classical)] and ^{4}He [blue square (RPMD) and orange pentagon (classical)] through (a) graphdiyne and (b) graphtriyne membranes with temperature T (in K).

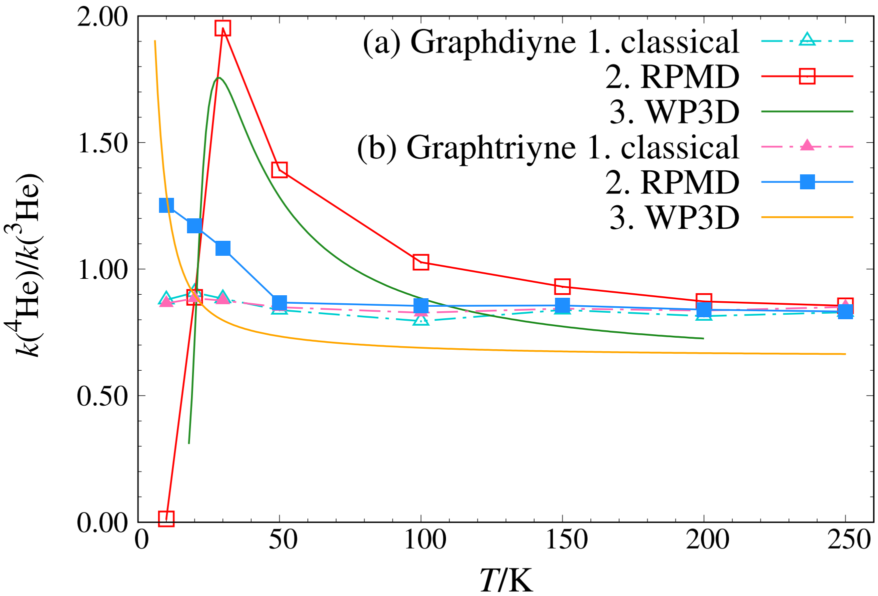

Fig. S9: Variation of the ^{4}He/^{3}He rate coefficient ratio, $k(^4\text{He})/k(^3\text{He})$, calculated using 1. classical (triangle) 2. ring polymer molecular dynamics, RPMD (square) and 3. three-dimensional wave packet propagation method, WP3D (circle) for the He transmission through (a) graphdiyne and (b) graphtriyne membranes with temperature T (in K).

Table S1: Summary of the rate calculations for ^{3}He and ^{4}He atom transmission through the graphdiyne (Gr2) and graphtriyne (Gr3) membranes at temperatures (T) 10, 20, 30, 50, 100, 150, 200, and 250 K: k_{QTST} (k_{TST}) − centroid-density quantum (classical) transition state theory rate coefficient;[a] κ_{RPMD} (κ_{cl}) − ring polymer (classical) transmission coefficient; k_{RPMD} (k_{cl}) − ring polymer (classical) molecular dynamics rate coefficient;[a] ^{4}He/^{3}He − ratio between the ^{4}He and ^{3}He rate coefficient.

	T/K	Isotope	classical				RPMD			
			k_{TST}	κ_{cl}	k_{cl}	^{4}He/^{3}He	k_{QTST}	κ_{RPMD}	k_{RPMD}	^{4}He/^{3}He
Gr2	10	^{3}He	3.80(-17)	1.00	3.80(-17)	0.88	3.97(-11)	0.63	2.51(-11)	0.01
		^{4}He	3.34(-17)	1.00	3.34(-17)		4.20(-13)	0.78	3.26(-13)	
	20	^{3}He	3.54(-4)	1.00	3.54(-4)	0.91	7.15(-7)	0.98	6.99(-7)	0.89
		^{4}He	3.21(-4)	1.00	3.21(-4)		6.25(-7)	0.99	6.21(-7)	
	30	^{3}He	6.09(0)	1.00	6.09(0)	0.88	4.53(-2)	0.99	4.52(-2)	1.95
		^{4}He	5.38(0)	1.00	5.38(0)		8.84(-2)	0.99	8.83(-2)	
	50	^{3}He	2.00(4)	1.00	2.00(4)	0.84	1.48(3)	1.00	1.48(3)	1.39
		^{4}He	1.68(4)	1.00	1.68(4)		2.06(3)	1.00	2.06(3)	
	100	^{3}He	1.84(7)	1.00	1.84(7)	0.80	4.10(6)	1.00	4.10(6)	1.03
		^{4}He	1.46(7)	1.00	1.46(7)		4.21(6)	1.00	4.21(6)	
	150	^{3}He	2.41(8)	1.00	2.41(8)	0.84	1.65(8)	1.00	1.65(8)	0.93
		^{4}He	2.02(8)	1.00	2.02(8)		1.54(8)	1.00	1.54(8)	
	200	^{3}He	1.03(9)	1.00	1.03(9)	0.81	8.07(8)	1.00	8.07(8)	0.87
		^{4}He	8.40(8)	1.00	8.40(8)		7.04(8)	1.00	7.04(8)	
	250	^{3}He	2.57(9)	1.00	2.57(9)	0.83	2.22(9)	1.00	2.22(9)	0.85
		^{4}He	2.14(9)	1.00	2.14(9)		1.90(9)	1.00	1.90(9)	
Gr3	10	^{3}He	4.36(11)	1.00	4.36(11)	0.86	8.59(10)	0.99	8.51(10)	1.25
		^{4}He	3.77(11)	1.00	3.77(11)		1.07(11)	0.99	1.06(11)	
	20	^{3}He	2.10(11)	1.00	2.10(11)	0.88	7.80(10)	0.99	7.79(10)	1.17
		^{4}He	1.86(11)	1.00	1.86(11)		9.13(10)	0.99	9.12(10)	
	30	^{3}He	1.00(11)	1.00	1.00(11)	0.88	5.19(10)	1.00	5.19(10)	1.08
		^{4}He	8.77(10)	1.00	8.77(10)		5.62(10)	1.00	5.62(10)	
	50	^{3}He	5.41(10)	1.00	5.41(10)	0.85	4.18(10)	1.00	4.18(10)	0.87
		^{4}He	4.60(10)	1.00	4.60(10)		3.63(10)	1.00	3.63(10)	
	100	^{3}He	5.29(10)	1.00	5.29(10)	0.83	4.84(10)	1.00	4.84(10)	0.86
		^{4}He	4.38(10)	1.00	4.38(10)		4.14(10)	1.00	4.14(10)	
	150	^{3}He	6.81(10)	1.00	6.81(10)	0.84	6.46(10)	1.00	6.46(10)	0.86
		^{4}He	5.74(10)	1.00	5.74(10)		5.53(10)	1.00	5.53(10)	
	200	^{3}He	8.58(10)	1.00	8.58(10)	0.84	8.16(10)	1.00	8.16(10)	0.84
		^{4}He	7.17(10)	1.00	7.17(10)		6.85(10)	1.00	6.85(10)	
	250	^{3}He	1.03(11)	1.00	1.03(11)	0.85	1.01(11)	1.00	1.01(11)	0.83
		^{4}He	8.74(10)	1.00	8.74(10)		8.38(10)	1.00	8.38(10)	

[a] The thermal coefficients are given in s^{-1} and the numbers in the parentheses denote powers of ten.