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RESEARCH ARTICLE

Transport properties of dilute D_2O vapour from first principles

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The classical kinetic theory of polyatomic gases has been applied to calculate the traditional transport properties of heavy water (D_2O) in the dilute gas limit using two highly accurate *ab initio* pair potentials. Results are reported for shear viscosity, thermal conductivity and the product of molar density and self-diffusion coefficient at temperatures between 250 and 2500 K. The expanded uncertainty (coverage factor $k = 2$) of the computed values is estimated to be 2% for viscosity and self-diffusion and 2% to 4%, depending on temperature, for thermal conductivity. For the most part, the agreement with the available experimental data is satisfactory.

Keywords: heavy water; kinetic theory; viscosity; thermal conductivity; self-diffusion

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1. Introduction

In a previous study [1], we investigated the transport and relaxation properties of ordinary water vapour in the dilute gas limit using the classical kinetic theory of polyatomic gases [2, 3] and four *ab initio* intermolecular potential energy surfaces for the H_2O molecule pair. The viscosity values calculated using the most accurate *ab initio* potential, the so-called CC-pol potential of Bukowski *et al.* [4, 5], agreed very well, within about 0.5%, with the best experimental data, whereas for the thermal conductivity systematic deviations from the experimental data of up to

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−5% were observed at higher temperatures. Using an improved kinetic theory approach, we recently obtained thermal conductivity values that are in excellent agreement with the experimental data at all temperatures [6]. In addition, a recent refinement [7] of our viscosity calculation resulted in deviations of only about 0.1% from the most accurate data, although this nearly exact match is most likely fortuitous since the expanded uncertainty (coverage factor $k = 2$, corresponding approximately to a 95% confidence level) of the calculated viscosity values was estimated to be 2%. All transport properties were calculated over a very wide temperature range, 250 to 2500 K, which significantly exceeds the temperature ranges for which experimental data are available. Thus, the calculated values can provide valuable guidance for the development of new transport property correlations.

In the present work, we extend these investigations to heavy water (D_2O) vapour. We report accurate values for shear viscosity, thermal conductivity and the product of molar density and self-diffusion coefficient for the same temperature range as in our work on dilute H_2O vapour and compare the results with the available experimental data.

2. Computational methods

In the kinetic theory of dilute polyatomic gases [2], the shear viscosity η in the dilute gas limit is given as

$$\eta = \frac{k_\mathrm{B}T}{\langle v \rangle} \frac{f_\eta^{(n)}}{\mathfrak{S}(2000)}, \tag{1}$$

where $\langle v \rangle = 4(k_\mathrm{B}T/\pi m)^{1/2}$ is the average relative thermal speed, k_B is Boltzmann's constant, m is the molecular mass, $\mathfrak{S}(2000)$ denotes a temperature-dependent generalised cross section and $f_\eta^{(n)}$ is the nth-order correction factor, which accounts for higher basis-function terms in the perturbation-series expansion of the solution of the Boltzmann equation [2]. Assuming that the vibrational states of the molecules do not change during collisions and that the influence of the vibrational motion on the trajectories is negligible, the thermal conductivity λ in the dilute gas limit can be written as a sum of a rigid-rotor contribution λ_rr and a vibrational contribution

λ_{vib} [6, 8, 9],

$$\lambda = \lambda_{\mathrm{rr}} + \lambda_{\mathrm{vib}}. \tag{2}$$

The rigid-rotor contribution is given as

$$\lambda_{\mathrm{rr}} = \frac{5k_{\mathrm{B}}^2 T}{2m\langle v\rangle} \frac{S_{11}^{(1)} - rS_{21}^{(1)} - rS_{12}^{(1)} + r^2 S_{22}^{(1)}}{S^{(1)}} f_{\lambda_{\mathrm{rr}}}^{(n)}, \tag{3}$$

where $S^{(1)}$ is a determinant of rigid-rotor cross sections,

$$S^{(1)} = \begin{vmatrix} \mathfrak{S}(1010)_{\mathrm{rr}} & \mathfrak{S}\binom{1010}{1001}_{\mathrm{rr}} \\ \mathfrak{S}\binom{1001}{1010}_{\mathrm{rr}} & \mathfrak{S}(1001)_{\mathrm{rr}} \end{vmatrix}, \tag{4}$$

and $S_{ij}^{(1)}$ are its minors. The dimensionless parameter r is given by

$$r = \left(\frac{2}{5}\frac{C_{\mathrm{rot}}}{k_{\mathrm{B}}}\right)^{1/2}, \tag{5}$$

where C_{rot} is the rotational contribution to the ideal gas heat capacity. The vibrational contribution to the thermal conductivity [6, 8, 9] can be written as

$$\lambda_{\mathrm{vib}} = N_{\mathrm{A}} C_{\mathrm{vib}} \rho_{\mathrm{m}} D_{\mathrm{self}}, \tag{6}$$

where N_{A} is Avogadro's constant, C_{vib} is the vibrational contribution to the ideal gas heat capacity, ρ_{m} is the molar density and D_{self} is the self-diffusion coefficient. Values of C_{vib} for D_2O were obtained from the ideal gas isobaric heat capacity C_p^0 as given by the equation of state of Herrig [10],

$$\begin{aligned} C_{\mathrm{vib}} &= C_p^0 - 4k_{\mathrm{B}} \\ &= k_{\mathrm{B}} \sum_{i=1}^{5} m_i \left(\frac{\theta_i}{T}\right)^2 \frac{\exp(-\theta_i/T)}{[\exp(-\theta_i/T) - 1]^2}, \end{aligned} \tag{7}$$

where $m_1 = 0.00863$, $m_2 = 0.97454$, $m_3 = 2.0646$, $m_4 = 0.23528$, $m_5 = 0.29555$, $\theta_1 = 274$ K, $\theta_2 = 1680$ K, $\theta_3 = 3875$ K, $\theta_4 = 7300$ K and $\theta_5 = 19000$ K. The product of molar density and self-diffusion coefficient is given in the dilute gas limit by

$$\rho_{\mathrm{m}} D_{\mathrm{self}} = \frac{k_{\mathrm{B}} T}{N_{\mathrm{A}} m\langle v\rangle} \frac{f_{D_{\mathrm{self}}}^{(n)}}{\sigma'(1000)}, \tag{8}$$

where $\sigma'(1000)$ is the self-part of the cross section $\mathfrak{S}(1000)$ [6]. In the present work, the higher-order correction factors $f_{\eta}^{(n)}$, $f_{\lambda_{\rm rr}}^{(n)}$ and $f_{D_{\rm self}}^{(n)}$ were evaluated up to $n = 3$, $n = 2$ and $n = 2$, respectively, using the expressions given in Refs. [6] and [11].

As in our previous work on H_2O [1, 6, 7], all required generalised cross sections were computed within the rigid-rotor approximation by means of the classical trajectory method using an extended version of the TRAJECT software code [3, 12]. For H_2O, the best agreement with the most accurate experimental data for shear viscosity was obtained using the CC-pol *ab initio* potential energy surface of Bukowski *et al.* [4, 5] for the trajectory calculations. However, as already noted in the Introduction, the excellent performance of the CC-pol potential is at least partly due to a fortuitous cancellation of errors. Whether or not such a cancellation also occurs for D_2O is difficult to ascertain because highly accurate experimental data for the transport properties of D_2O are scarce. We therefore decided to use, in addition to the CC-pol potential, the more accurate CC-pol-8s potential of Cencek *et al.* [13]. It was fitted to the same set of *ab initio* interaction energies as CC-pol, but uses a more flexible functional form for the analytical potential function. This results in a significantly better fit, with the root mean square error being reduced by about a factor of four [13].

The CC-pol potential was developed for rigid H_2O molecules in their zero-point vibrationally averaged (ZPVA) geometry. While the equilibrium geometries for H_2O and D_2O are identical within the Born-Oppenheimer approximation, the ZPVA geometries differ. To accurately determine the differences, we performed a geometry optimization using the frozen-core CCSD(T) [14] method with the cc-pVQZ [15] basis set, followed by cubic force field calculations for H_2O and D_2O at the same level of theory. The calculations were performed using the CFOUR program [16]. We obtained an equilibrium bond length of 95.79 pm and an equilibrium bond angle of 104.1°. The respective ZPVA values obtained are 97.26 pm and 104.0° for H_2O and 96.86 pm and 104.0° for D_2O. Thus, the ZPVA bond length in D_2O differs by only −0.4 pm from that in H_2O, and the value of the ZPVA bond angle is practically the same for both molecules. It is therefore justified to employ an intermolecular potential energy surface developed using the ZPVA geometry of H_2O, such as CC-pol or CC-pol-8s, also for D_2O.

The CC-pol and CC-pol-8s potential functions were slightly modified as de-

scribed in Ref. [1] to avoid unphysical behavior at very small intermolecular separations. This modification does not negatively impact the accuracy of the calculated transport property values at the temperatures considered in this work.

The classical trajectories describing collisions between two rigid D_2O molecules were obtained by integrating Hamilton's equations for asymmetric tops from pre- to post-collisional values. The initial and final separation was set to 100 nm. Total-energy-dependent generalised cross sections in the centre-of-mass frame, which are 13-dimensional integrals over the initial states of the trajectories [3], were calculated for 25 values of the total energy, $E = E_{\mathrm{tr}} + E_{\mathrm{rot}}$, in the range from 160 to 50,000 K by means of a simple Monte Carlo procedure utilizing quasi-random numbers. Up to 400,000 trajectories were computed at each total energy value. For energies below 1000 K, the number of trajectories had to be reduced because the computational demand required to calculate the trajectories with sufficient accuracy increases as the energy decreases. For instance, only 30,000 trajectories were calculated at 160 K. However, the contributions of such low energies to the transport properties of heavy water vapour at temperatures above 250 K are negligibly small. An integration over the total energy, which was performed using Chebyshev quadrature, yielded temperature-dependent generalised cross sections in the centre-of-mass frame [3]. Finally, the centre-of-mass cross sections were converted to laboratory frame cross sections [3, 17].

3. Results and discussion

The transport property values calculated using the CC-pol-8s potential are listed for 78 temperatures in the range from 250 to 2500 K in Table 1.

3.1. *Higher-order correction factors*

In Figure 1, the higher-order correction factors $f_\eta^{(3)}$, $f_\eta^{(2)}$, $f_{\lambda_{\mathrm{rr}}}^{(2)}$ and $f_{D_{\mathrm{self}}}^{(2)}$ obtained with the CC-pol-8s potential are shown as a function of temperature. The correction factors computed using the CC-pol potential are not shown because they do not differ significantly. Deviations of the correction factors from unity do not exceed 1%, and the ratio $f_\eta^{(3)}/f_\eta^{(2)}$ differs from unity by at most 0.02%. The higher-order correction factors for H_2O [6, 7] are shown in the figure for comparison. They

Table 1. Viscosity η, thermal conductivity λ and product of molar density and self-diffusion coefficient, $\rho_m D_{self}$, of D_2O vapour in the dilute gas limit calculated using the CC-pol-8s potential of Cencek *et al.* [13].

T (K)	$10^6 \times \eta$ (Pa s)	$10^3 \times \lambda$ (W m^{-1} K^{-1})	$10^4 \times \rho_m D_{self}$ (mol m^{-1} s^{-1})	T (K)	$10^6 \times \eta$ (Pa s)	$10^3 \times \lambda$ (W m^{-1} K^{-1})	$10^4 \times \rho_m D_{self}$ (mol m^{-1} s^{-1})
250	8.359	14.39	5.052	740	28.15	64.56	19.18
260	8.703	15.06	5.287	760	29.00	67.28	19.79
270	9.049	15.75	5.525	780	29.85	70.03	20.38
273.15	9.158	15.97	5.601	800	30.69	72.82	20.98
280	9.397	16.45	5.767	820	31.53	75.63	21.56
290	9.748	17.16	6.011	840	32.37	78.47	22.15
298.15	10.04	17.75	6.214	860	33.20	81.33	22.73
300	10.10	17.88	6.260	880	34.02	84.22	23.31
310	10.46	18.62	6.511	900	34.84	87.12	23.88
320	10.82	19.38	6.766	920	35.65	90.04	24.44
330	11.18	20.14	7.025	940	36.45	92.98	25.00
340	11.55	20.93	7.286	960	37.25	95.93	25.56
350	11.92	21.73	7.551	980	38.04	98.88	26.11
360	12.30	22.54	7.819	1000	38.82	101.9	26.66
370	12.67	23.37	8.091	1050	40.76	109.3	28.00
380	13.05	24.22	8.365	1100	42.65	116.8	29.32
390	13.44	25.08	8.642	1150	44.50	124.3	30.60
400	13.83	25.95	8.923	1200	46.31	131.7	31.86
410	14.22	26.85	9.205	1250	48.08	139.2	33.09
420	14.61	27.75	9.490	1300	49.82	146.6	34.30
430	15.01	28.68	9.778	1350	51.52	153.9	35.48
440	15.41	29.62	10.07	1400	53.19	161.2	36.64
450	15.82	30.57	10.36	1450	54.83	168.4	37.78
460	16.22	31.54	10.65	1500	56.44	175.6	38.90
470	16.63	32.53	10.95	1550	58.02	182.7	40.00
480	17.04	33.53	11.25	1600	59.57	189.8	41.09
490	17.46	34.55	11.55	1650	61.10	196.7	42.16
500	17.87	35.58	11.85	1700	62.61	203.6	43.21
520	18.71	37.70	12.45	1750	64.09	210.5	44.24
540	19.56	39.87	13.06	1800	65.55	217.3	45.27
560	20.41	42.10	13.67	1850	66.99	224.0	46.28
580	21.26	44.39	14.29	1900	68.41	230.6	47.27
600	22.12	46.74	14.90	1950	69.82	237.2	48.26
620	22.98	49.14	15.52	2000	71.21	243.7	49.23
640	23.85	51.59	16.13	2100	73.94	256.6	51.15
660	24.71	54.10	16.75	2200	76.61	269.3	53.03
680	25.57	56.65	17.36	2300	79.23	281.7	54.88
700	26.43	59.24	17.97	2400	81.80	293.9	56.69
720	27.29	61.89	18.58	2500	84.32	306.0	58.48

exhibit similar temperature dependences as the correction factors for D_2O, but are on average somewhat smaller.

3.2. *Uncertainty budget*

The standard uncertainties of the calculated viscosity values at 250 K due to the use of the rigid-rotor approximation, the neglect of quantum effects, deficiencies of the CC-pol-8s potential (which are mainly due to the use of the ZPVA geometry of H_2O instead of that for D_2O), the inaccuracy of the Monte Carlo integration and the use

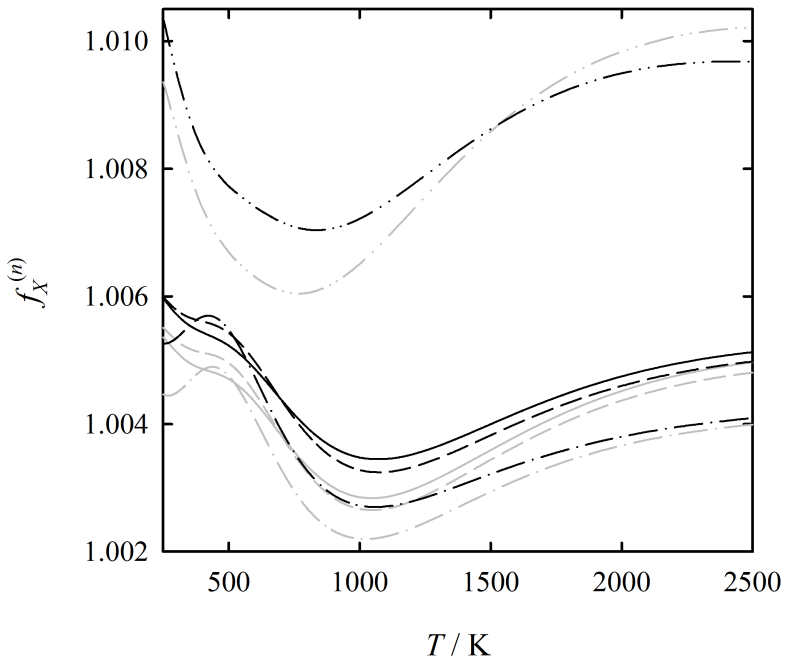

Figure 1. Higher-order correction factors $f_X^{(n)}$ for D_2O (black lines) and H_2O (gray lines): ——, $f_\eta^{(3)}$; – – –, $f_\eta^{(2)}$; –··–, $f_{\lambda_{\rm rr}}^{(2)}$; –·–, $f_{D_{\rm self}}^{(2)}$.

of the third-order kinetic theory approximation are estimated to be of the order of 0.5%, 0.3%, 0.7%, 0.15% and 0.02%, respectively. The resulting combined expanded (k = 2) uncertainty is approximately 2%. The relative error caused by the use of the rigid-rotor approximation probably increases somewhat with temperature, but the relative error caused by the neglect of quantum effects certainly decreases with temperature. Therefore, our estimate for the relative combined expanded uncertainty at 250 K should be valid for the whole temperature range from 250 to 2500 K.

For the self-diffusion coefficient, the standard uncertainty due to the use of only the second-order kinetic theory approximation is estimated to be of the order of 0.1%, whereas the other relative uncertainty contributions should be similar to those for viscosity. The resulting combined expanded uncertainty is again approximately 2%.

For the thermal conductivity at 250 K, the relative uncertainty contributions should be similar to those for the self-diffusion coefficient. However, in contrast to viscosity and self-diffusion, the thermal conductivity should also be appreciably affected by vibrationally inelastic and vibrationally resonant collisions, which are

not accounted for in the classical trajectory calculations. The probability for such collisions to occur increases with temperature as higher vibrational energy levels become populated. A further uncertainty contribution arises from the uncertainty of the C_{vib} values calculated via Equation (7). Herrig [10] obtained the coefficients of this equation from a fit to the only available C_p^0 values for D_2O, which were calculated by Friedman and Haar [18] using statistical mechanics. Friedman and Haar did not provide uncertainty estimates, but their H_2O values from the same paper deviate by at most 0.8% for temperatures up to 2500 K from more recent C_p^0 values [19]. When more accurate C_p^0 values for D_2O become available, the thermal conductivity can easily be re-evaluated utilizing the tabulated $\rho_{\mathrm{m}} D_{\mathrm{self}}$ values and Equations (2), (6) and (7). Due to the additional uncertainty contributions, the combined expanded uncertainty of the calculated thermal conductivity values is larger than 2% at elevated temperatures. We estimate it to be 3% between 600 and 1500 K and 4% above 1500 K.

Note that our uncertainty estimates for the transport properties do not take into account partial dissociation of D_2O at high temperatures.

3.3. *Comparison with experimental data*

In Figure 2, the viscosity values calculated using the CC-pol-8s potential are compared with the few available experimental data [20–24], the current correlation of the International Association for the Properties of Water and Steam (IAPWS) from 2007 [25–27] and the values computed using the CC-pol potential. Rowlinson [20] only provided the ratio of the D_2O and H_2O viscosities for three temperatures with a claimed uncertainty of 1%. We converted these ratios to D_2O viscosities using the recent dilute gas viscosity correlation for H_2O of Hellmann and Vogel [7], which has an expanded ($k = 2$) uncertainty of 0.4% at these temperatures. Bonilla *et al.* [21] measured the viscosities of argon, water vapour and heavy water vapour at atmospheric pressure. Since their viscosity data for all three gases are systematically too low, we re-evaluated their D_2O viscosities using highly accurate *ab initio* viscosity values for argon [28] and the ratios of their measured D_2O and Ar viscosities. We also extrapolated the results to the limit of zero density using the density dependence of the IAPWS 2007 correlation. The data of Timrot *et al.* [22], which have a stated uncertainty of only 0.35%, and the data of Agayev [24] were

extrapolated to the limit of zero density using the published isothermal values as a function of pressure, whereas Abe *et al.* [23] provided values for the dilute gas limit in their paper. As can be seen in Figure 2, the experimental data, except for two data points of Rowlinson [20], are consistent with the values computed using the CC-pol-8s potential. The agreement with the values for the CC-pol potential is only slightly inferior. Above room temperature, the IAPWS 2007 correlation, which is valid from 277 to 775 K, and the values calculated for the CC-pol-8s potential agree within 1.1%. Below room temperature, where no experimental data are available, the deviations from the calculated values increase to +8% at 250 K.

Figure 3 shows the ratios of the D_2O and H_2O viscosities of Rowlinson [20], Bonilla *et al.* [21] and Timrot *et al.* [22], as well as the viscosity ratios obtained using the CC-pol-8s and CC-pol potentials for D_2O and the CC-pol potential for H_2O. Also shown is the ratio of the zero-density contributions of the current IAPWS correlations for D_2O [25–27] and H_2O [29, 30] and the ratio one would obtain if the intermolecular interactions in both D_2O and H_2O vapour are approximated by a single spherically symmetric potential function,

$$\frac{\eta^{\mathrm{sph}}_{\mathrm{D_2O}}}{\eta^{\mathrm{sph}}_{\mathrm{H_2O}}} = \left(\frac{m_{\mathrm{D_2O}}}{m_{\mathrm{H_2O}}}\right)^{1/2} \approx 1.054. \tag{9}$$

We note that the well-known Mason-Monchick approximation (MMA) [31, 32] yields the same constant ratio (assuming, of course, that the same intermolecular potential is used for both gases). At the highest temperatures, the actual viscosity ratio should be close to $\eta^{\mathrm{sph}}_{\mathrm{D_2O}}/\eta^{\mathrm{sph}}_{\mathrm{H_2O}}$. This is indeed the case for the ratio of the computed D_2O and H_2O viscosities, which is only 1.3% smaller than $\eta^{\mathrm{sph}}_{\mathrm{D_2O}}/\eta^{\mathrm{sph}}_{\mathrm{H_2O}}$ at 2500 K. However, the ratio of the IAPWS correlations is 5.9% smaller at 2500 K. This is caused by the incorrect high-temperature extrapolation behavior of the IAPWS 2008 viscosity correlation for H_2O, see Refs. [1] and [7] for details.

In Figure 4, the thermal conductivity values computed using the CC-pol-8s potential are compared with the available experimental data [33–43], the IAPWS 2007 correlation [25–27] and the values computed using the CC-pol potential. Not all experimenters derived thermal conductivity values for the limit of zero density. In these cases, we used either the density dependence of the IAPWS 2007 correlation

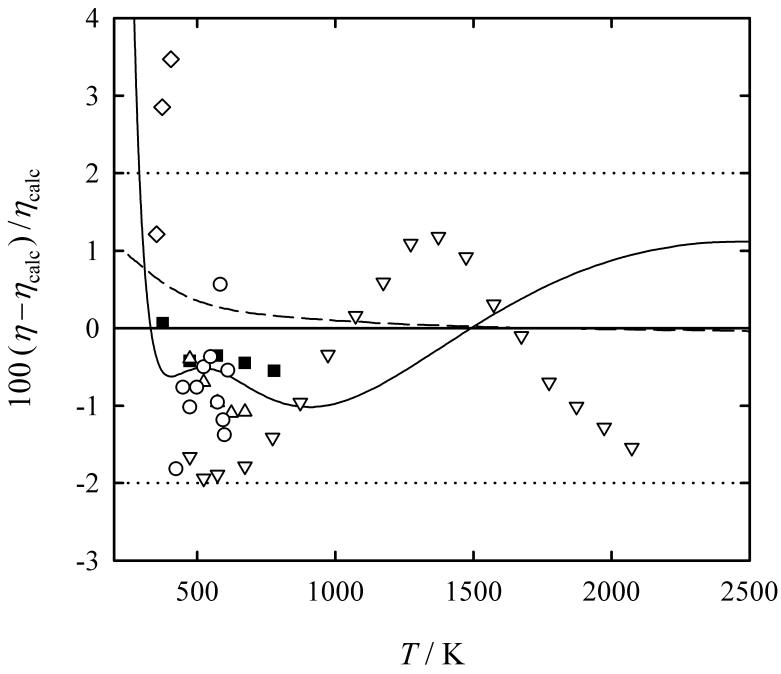

Figure 2. Relative deviations of experimental data, an experimentally based correlation and calculated values for the viscosity of D_2O in the dilute gas limit from values computed using the CC-pol-8s potential: ◇, Rowlinson [20]; ▽, Bonilla *et al.* [21], reanalysed; ■, Timrot *et al.* [22]; △, Abe *et al.* [23]; ○, Agayev [24]; ——, IAPWS 2007 correlation [25–27]; – – –, values obtained using the CC-pol potential; · · · · · ·, uncertainty range (k = 2) of the computed values.

or, where available, isothermal values as a function of pressure to obtain values for the zero-density limit. The agreement between the experimental data, which exhibit considerable scatter, and the calculated values for both intermolecular potentials is satisfactory, particularly at higher temperatures. The IAPWS 2007 correlation, which is valid from 277 to 825 K, is shown only for temperatures up to 1000 K in the figure because it exhibits unphysical behavior at higher temperatures due to its mathematical structure (fifth-order polynomial in temperature). It deviates by +1.0% to +2.3% and +0.4% to +1.6% from the values computed using the CC-pol-8s and CC-pol potentials, respectively.

Several groups have measured the thermal conductivities of both D_2O and H_2O vapour with the same apparatus at similar temperatures [33–37, 40, 41, 43–45]. The resulting ratios are shown in Figure 5. Also plotted in the figure are the ratios obtained using the CC-pol-8s and CC-pol potentials for D_2O and the CC-pol potential for H_2O as well as the ratio of the zero-density contributions of the current IAPWS correlations for D_2O [25–27] and H_2O [46, 47]. There is noticeably

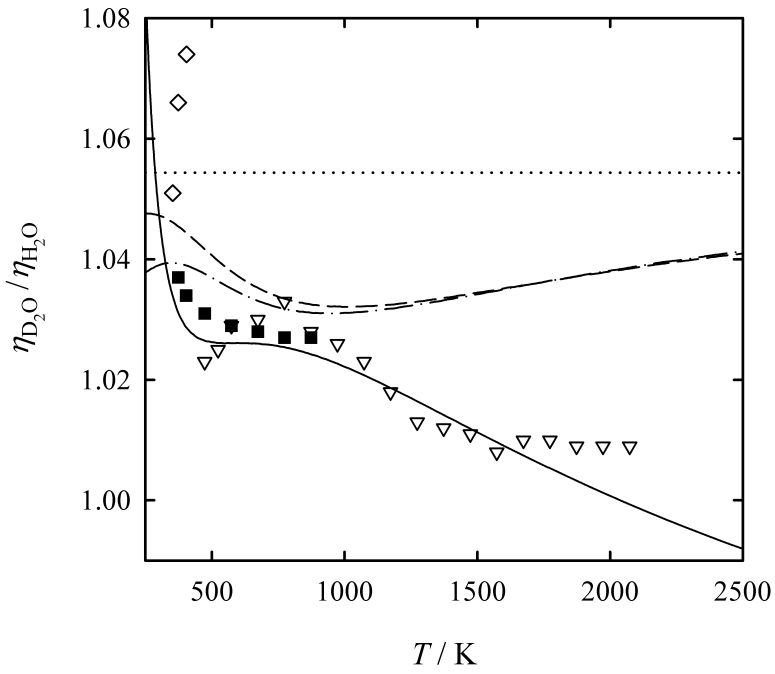

Figure 3. Ratio of the viscosities of D_2O and H_2O in the dilute gas limit: ◇, Rowlinson [20]; ▽, Bonilla *et al.* [21]; ■, Timrot *et al.* [22]; ——, ratio obtained from the current IAPWS correlations [25–27, 29, 30]; – · –, ratio obtained using the CC-pol-8 potential for D_2O and the CC-pol potential for H_2O; – – –, ratio obtained using the CC-pol potential for both D_2O and H_2O; · · · · · ·, $\eta^{\rm sph}_{D_2O}/\eta^{\rm sph}_{H_2O}$.

less scatter in the experimental ratios than in the thermal conductivity data for each of the two gases since systematic measurement errors partly cancel. The ratio of the calculated values agrees very well with most of the experimental ratios. It strongly increases up to about 1000 K, which is mainly due to the ideal gas heat capacity of D_2O increasing faster than that of H_2O. The ratio then decreases slowly with temperature as the heat capacities approach their classical limit.

There are no experimental data for the self-diffusion coefficient of dilute D_2O vapour with which to compare. The computed ratio $D_{\rm self,D_2O}/D_{\rm self,H_2O}$, at a given molar density $\rho_{\rm m}$, is within 1% of the ratio η_{H_2O}/η_{D_2O} at all temperatures. For a spherically symmetric potential (as well as within the MMA), both ratios would be identical,

$$\frac{D^{\rm sph}_{\rm self,D_2O}}{D^{\rm sph}_{\rm self,H_2O}} = \frac{\eta^{\rm sph}_{H_2O}}{\eta^{\rm sph}_{D_2O}} = \left(\frac{m_{H_2O}}{m_{D_2O}}\right)^{1/2} \approx 0.948, \tag{10}$$

which follows from Equations (1) and (8).

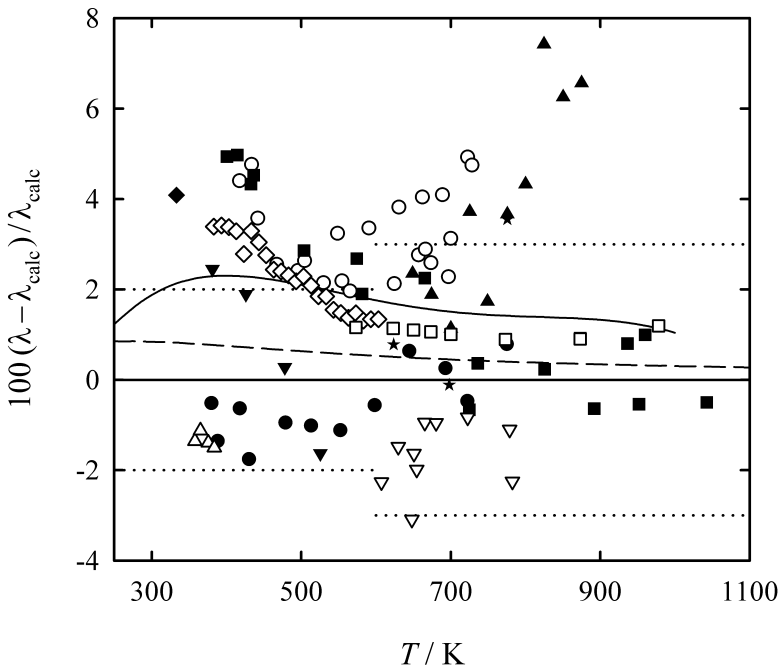

Figure 4. Relative deviations of experimental data, an experimentally based correlation and calculated values for the thermal conductivity of D_2O in the dilute gas limit from values computed using the CC-pol-8s potential: ○, Vargaftik and Oleshchuk [33]; ●, Vargaftik and Zaitseva [34]; ▼, Baker and Brokaw [35]; ◇, Le Neindre *et al.* [36]; ◆, Dijkema *et al.* [37]; ■, Vargavtik *et al.* [38]; ★, Tarzimanov and Zainullin [39]; ▲, Amirkhanov *et al.* [40]; △, Curtiss *et al.* [41]; ▽, Tufeu *et al.* [42]; □, Tarzimanov and Gabitov [43]; ——, IAPWS 2007 correlation [25–27]; – – –, values obtained using the CC-pol potential; · · · · · · , uncertainty range (k = 2) of the computed values.

4. Summary

The traditional transport properties of heavy water vapour in the dilute gas limit have been determined using highly accurate *ab initio* pair potentials and the best available kinetic theory. Values for shear viscosity, thermal conductivity and the product of molar density and self-diffusion coefficient have been computed for 78 temperatures from 250 to 2500 K. For viscosity and self-diffusion, the expanded uncertainty (coverage factor k = 2) of the computed values is estimated to be 2% at all temperatures. For thermal conductivity, the estimated expanded uncertainty is 2% below 600 K, 3% between 600 and 1500 K and 4% above 1500 K. These estimates do not take into account partial dissociation at higher temperatures.

Experimental data in the dilute gas phase are only available for viscosity and thermal conductivity. The agreement with the calculated values is, for the most part, satisfactory. Furthermore, the ratios η_{D_2O}/η_{H_2O} and $\lambda_{D_2O}/\lambda_{H_2O}$ determined from the calculated viscosity and thermal conductivity values of the present work

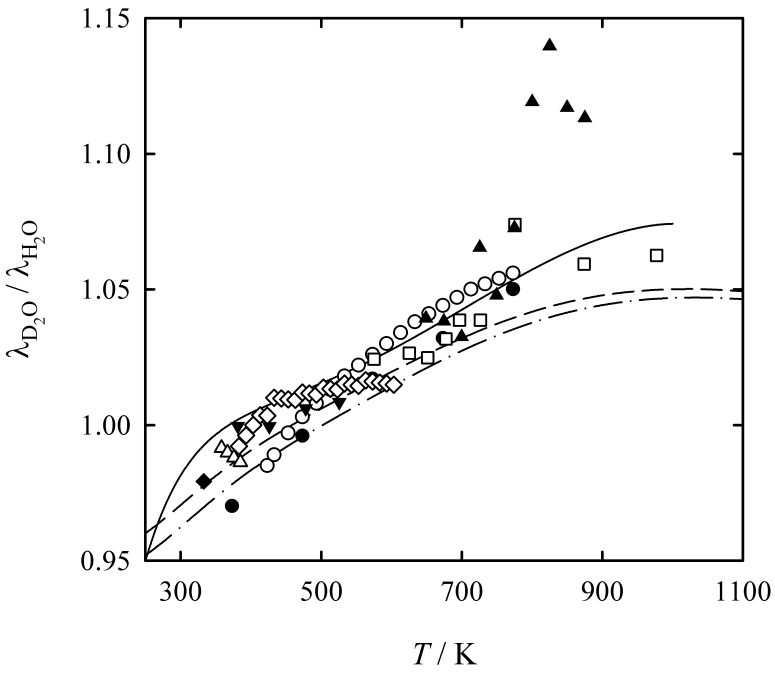

Figure 5. Ratio of the thermal conductivities of D_2O and H_2O in the dilute gas limit: ○, Vargaftik and Oleshchuk [33]; ●, Vargaftik and Zaitseva [34]; ▼, Baker and Brokaw [35]; ◇, Le Neindre *et al.* [36]; ◆, Dijkema *et al.* [37]; ▲, Amirkhanov *et al.* [40, 44]; △, Curtiss *et al.* [41]; □, Tarzimanov and Gabitov [43, 45]; ——, ratio obtained from the current IAPWS correlations [25–27, 46, 47]; – · –, ratio obtained using the CC-pol-8 potential for D_2O and the CC-pol potential for H_2O; – – –, ratio obtained using the CC-pol potential for both D_2O and H_2O.

and of our recent work on H_2O [6, 7] agree very well with the ratios obtained from experimental data.

The present results can provide useful guidance for the development of new reference correlations for the viscosity and thermal conductivity of heavy water.

Disclosure statement

No potential conflict of interest was reported by the authors.

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