

Calculation of the transport and relaxation properties of dilute water vapor

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Transport properties of dilute water vapor have been calculated in the rigid-rotor approximation using four different potential energy hypersurfaces and the classical-trajectory method. Results are reported for shear viscosity, self-diffusion, thermal conductivity, and volume viscosity in the dilute-gas limit for the temperature range of 250–2500 K. Of these four surfaces the CC-pol surface of Bukowski *et al.* [J. Chem. Phys. **128**, 094314 (2008)] is in best accord with the available measurements. Very good agreement is found with the most accurate results for viscosity in the whole temperature range of the experiments. For thermal conductivity the deviations of the calculated values from the experimental data increase systematically with increasing temperature to around 5% at 1100 K. For both self-diffusion and volume viscosity, the much more limited number of available measurements are generally consistent with the calculated values, apart from the lower temperature isotopically labeled diffusion measurements. © 2009 American Institute of Physics. [DOI: 10.1063/1.3158830]

I. INTRODUCTION

The formal kinetic theory for dilute gaseous systems¹ describes their transport and relaxation properties in terms of generalized cross sections. These cross sections are determined by the dynamics of binary collisions, which are governed by the intermolecular potential energy hypersurface, characteristic of the specific molecular interaction.

Transport and relaxation properties of dilute simple molecular gases can be calculated directly nowadays from their intermolecular potential with an accuracy comparable to that of the best available experimental data, see, for example, Refs. 2–11. The comparison between the calculated and the best experimental values provides a unique and stringent test of the accuracy of the potential surface. At low and high temperatures, where experimental data are of lower accuracy or nonexistent, calculations provide an accurate and reliable way of estimating transport and relaxation properties.

Ideally a quantum-mechanical description should be employed for the calculation of the generalized cross sections. However, for molecule-molecule systems this is at present not computationally feasible, apart possibly for pure hydrogen. For the temperatures relevant to the present work (250–2500 K), the method of choice is a classical-trajectory calculation, which is computationally relatively efficient and at the same time accurate. This was tested and confirmed by detailed comparison with quantum calculations for the He–N₂ system.^{12,13} In addition, the accuracy of the classical-trajectory method has recently been supported by computations of the viscosity of carbon dioxide⁷ and methane,¹⁰ for which close agreement with highly accurate viscosity measurements near room temperature has been obtained.

The work presented in this paper is a continuation of our previous studies^{7–11} and aims to improve our knowledge of transport and relaxation properties. So far we have confined our calculations to dilute gases consisting of linear or spherical top and nonpolar or weakly polar molecules. Water is the first asymmetric top, strongly polar, molecule for which classical-trajectory calculations have ever been performed with a full-dimensional rigid-molecule potential surface. As such the present work represents a significant step forward in our ability to calculate accurately transport and relaxation properties.

Water vapor is relevant in a particularly wide variety of both engineering and scientific contexts. For instance, it is used as working fluid in steam turbines, it is used for energy storage, it is a significant greenhouse gas whose effects must be included in climate modeling, and water masers have been observed in the interstellar medium. The accuracy of available shear viscosity and thermal conductivity data for water vapor, see Sec. IV below, is generally very good at lower temperatures. At higher temperatures, relevant for steam turbines, only very few data sets exist and these have relatively large uncertainties.

In the present paper we report on calculations of the shear viscosity, the thermal conductivity, the self-diffusion coefficient, and the volume viscosity of dilute water vapor. The relevant generalized cross sections have been evaluated by means of classical-trajectory calculations directly from accurate intermolecular potential energy hypersurfaces. For linear molecules the working expressions for the generalized cross sections in terms of properties of individual trajectories were derived by Curtiss.¹⁴ The extension to rigid asymmetric tops (such as water) has been provided.¹⁵

We have used four different intermolecular potentials for the H₂O–H₂O interaction: SAPT-5s¹⁶ and SAPT-5st,¹⁷ based

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on symmetry-adapted perturbation theory (SAPT),¹⁸ SDFT-5s,¹⁹ based on SAPT(DFT),²⁰ which used density-functional theory (DFT) for the description of the monomers, and CC-pol,^{21–23} based on supermolecular MP2 (second-order Møller–Plesset perturbation theory) and CCSD(T) (coupled-cluster theory with iterative single and double excitations and noniterative perturbation treatment of triple excitations)²⁴ calculations. Of these four potentials, CC-pol is the most recent and most accurate and was tested for a number of properties (such as second pressure virial coefficients and rovibrational spectra of dimers), but not yet for transport and relaxation properties.

As we were completing our calculations a new potential, CC-pol-8s,²⁵ has become available. Although its accuracy is deemed slightly better than that of CC-pol, attested by a better description of the rovibrational spectra, the improvement in accuracy has not been judged sufficient to justify performing a new set of classical trajectories, which would be computationally expensive due to the much more complex expressions for the potential. The CC-pol-8s potential was therefore not considered in the present study.

All interaction potentials considered were developed using rigid monomers in the zero-point vibrationally averaged structure. The deepest well in the CC-pol potential surface has a depth of 1783 cm⁻¹, and this system has much stronger long-range (dipole-dipole) interactions than any considered previously.

It was shown^{7,10} that results using the rigid-rotor assumption are consistent with experiment for the viscosity and self-diffusion coefficients of carbon dioxide and methane up to very high temperatures. However, for thermal conductivity the neglect of energy transport by vibrationally excited molecules becomes more questionable. In order to estimate the influence on the thermal conductivity of neglecting vibration, we have employed the approximation described in our previous work.^{6–9,11} Hence we have corrected, where necessary, the generalized cross sections obtained from the classical-trajectory calculations based on the rigid-rotor assumption. For carbon dioxide and methane, which are more vibrationally active than water, the approximate procedure for the inclusion of the effects of the vibrational degrees of freedom has been shown to produce good agreement with the available experimental data on the thermal conductivity and the thermomagnetic effect.^{9,11}

II. THEORY

A. Transport properties

The shear viscosity η , the self-diffusion coefficient D , and the thermal conductivity λ of a polyatomic gas in the limit of zero density and in the absence of external fields can be expressed as^{1,26}

$$[\eta]_n = \frac{k_B T}{\langle v \rangle_0} \frac{f_\eta^{(n)}}{\mathfrak{S}(2000)}, \quad (1)$$

$$[D]_n = \frac{k_B T}{nm \langle v \rangle_0} \frac{f_D^{(n)}}{\mathfrak{S}'(1000)}, \quad (2)$$

$$[\lambda]_n = \frac{5k_B^2 T}{2m \langle v \rangle_0} \frac{\mathfrak{S}(1001) - 2r \mathfrak{S}\left(\begin{smallmatrix} 1001 \\ 1010 \end{smallmatrix}\right) + r^2 \mathfrak{S}(1010)}{\mathfrak{S}(1010)\mathfrak{S}(1001) - \mathfrak{S}\left(\begin{smallmatrix} 1001 \\ 1010 \end{smallmatrix}\right)^2} f_\lambda^{(n)}, \quad (3)$$

where $\langle v \rangle_0 = 4(k_B T / \pi m)^{1/2}$ is the average relative thermal speed, n is the number density, m is the molecular mass, T is the temperature, and k_B is Boltzmann's constant. The quantities $\mathfrak{S}(2000)$, $\mathfrak{S}'(1000)$, $\mathfrak{S}(1010)$, $\mathfrak{S}(1001)$, and $\mathfrak{S}\left(\begin{smallmatrix} 1001 \\ 1010 \end{smallmatrix}\right)$ are generalized cross sections, and the notation and conventions employed are fully described elsewhere.^{1,10} The parameter r is given by

$$r = \left(\frac{2 c_{\text{int}}}{5 k_B} \right)^{1/2}, \quad c_{\text{int}} = c_{\text{rot}} + c_{\text{vib}}. \quad (4)$$

Here c_{int} is the contribution of both the rotational, c_{rot} , and the vibrational, c_{vib} , degrees of freedom to the isochoric heat capacity, c_V .

The quantities $f_\eta^{(n)}$, $f_D^{(n)}$, and $f_\lambda^{(n)}$ are n th-order correction factors and account for the effects of higher basis-function terms in the perturbation-series expansion of the solution of the Boltzmann equation.¹ In this work we consider the second-order approximations for viscosity and thermal conductivity, but only the first-order approximation for self-diffusion ($f_D^{(n)} = 1$), as no higher-order expressions are available. Contributions from both velocity coupling^{1,27} and angular-momentum coupling^{1,28,29} are included in the second-order approximations.

B. Volume viscosity

The volume viscosity (also known as the bulk viscosity) can be inferred from measurements of the absorption and dispersion of ultrasonic waves in the gas.¹ As noted in Ref. 30, for the analysis of sound-absorption measurements the volume viscosity η_V is the fundamental quantity of interest. In this work we limit our investigation to the contribution to volume viscosity that arises from rotational relaxation only, as the nature of the intermolecular potential used in the calculation precludes investigation of the vibrational relaxation process.

The volume viscosity can be written as

$$[\eta_V]_n = \frac{k_B c_{\text{int}}}{c_V^2} \frac{k_B T}{\langle v \rangle_0 \mathfrak{S}(0001)} f_{\eta_V}^{(n)}. \quad (5)$$

The quantity $f_{\eta_V}^{(n)}$ is the n th-order correction factor for the volume viscosity and accounts for the effects of higher basis-function terms in the perturbation-series expansion of the solution of the Boltzmann equation.¹ The explicit expression for the second-order kinetic theory expression, $[\eta_V]_2$, is given by Ref. 31.

A number of experimenters have presented their measurements of sound absorption and dispersion in terms of a rotational relaxation time τ_{exp} or the corresponding rotational relaxation rate or as a rotational collision number.

We have converted from the relaxation time or rate measurements to volume viscosity values using the first-order kinetic theory relation,¹

$$[\eta_V]_1 = \frac{k_B c_{\text{int}} P \tau_{VT}}{c_V^2},$$

$$[\eta_V]_n \approx \frac{k_B c_{\text{int}} P \tau_{\text{exp}}}{c_V^2},$$
(6)

where τ_{VT} is the isothermal relaxation time.^{30,32} Use of this equation to convert measured relaxation times or rates to volume viscosity values is only approximately equivalent to analyzing the measurements in terms of the volume viscosity. For collision-number results we have first used the standard relation^{1,9} with the rotational relaxation time.

III. CLASSICAL-TRAJECTORY CALCULATIONS

The classical-trajectory calculations were performed using an extension of the TRAJECT software code for linear molecules,³³ previously employed for pure nitrogen, carbon monoxide, and carbon dioxide (Refs. 7–9 and references therein). This code has been modified³⁴ to allow for the additional variables and averaging needed for rigid asymmetric tops and has recently been successfully used for pure methane.^{10,11}

The water molecule was represented in the trajectory calculations as a rigid asymmetric top. The geometry of the monomers corresponds to the zero-point vibrationally averaged structure used for the determination of the four interaction potentials considered in this work. For a given total energy, translational plus rotational, classical trajectories describing the collision of two molecules were obtained by integrating Hamilton's equations from pre- to postcollisional values (initial and final separation of 500 Å). We have used all four potentials as published for distances up to 500 Å. The fits employed included the long-range behavior correctly.

The total-energy-dependent generalized cross sections can be represented as 13-dimensional integrals, which were evaluated by means of a Monte Carlo procedure. The initial values of the momenta for the relative motion and for the rotation of the two molecules, as well as the angles defining their relative orientation, were chosen using a pseudorandom number generator.

At very small intermolecular distances the fits to the four potential surfaces yield highly negative potential energies. This unphysical behavior would cause numerical problems in the trajectory calculations for very high collision energies, those above about 20 000 K. (For convenience in the context of temperature-dependent observables we quote energies of interest as the equivalent temperatures.) To avoid this problem all potentials were augmented by an extremely short-ranged, highly repulsive, additional term of the form $V_{\text{rep}}(R) = (2.15 \text{ Å}/R)^{100} \text{ K}$. The value of 2.15 Å was found to be large enough to ensure that the potential energy always increases as the intermolecular separation decreases but

small enough to ensure that, to the accuracy of our calculations, this term does not influence the values of the thermally averaged cross sections up to 2500 K.

The classical trajectories were determined at 25 values of the total energy, divided into three ranges. In each range the energy values were chosen as the pivot points for Chebyshev interpolation in order to facilitate calculations of the cross sections at a number of temperatures.^{34,35} The highest energy used was 50 000 K, which is more than sufficient for the temperature range considered in this work. At each energy up to 100 000 classical trajectories (80 000 for CC-pol) were evaluated. The number of trajectories had to be reduced towards lower energies, those comparable or less than the well depth, because the low-energy trajectories require much longer computing times. For example, at 120 K, the lowest energy considered for SAPT-5s, SAPT-5st, and SDFT-5s, only 12 000 trajectories were calculated. For CC-pol the lowest energy was 200 K with 6000 trajectories. The smaller number of trajectories and the higher minimum energy for CC-pol was necessary because this potential function, in contrast to the other potentials used, is polarizable and thus requires more computing time for the evaluation of the potential and its derivatives. Contributions to the cross sections from trajectories with collision energies below 200 K were found to be totally negligible for all temperatures considered because they have only a very small weight in the thermal averaging process. Also the much smaller number of trajectories at low energies has negligible influence on the uncertainty of the calculated cross sections.

The precision of the calculations was assessed by estimating the convergence of the final temperature-dependent generalized cross sections as a function of the number of trajectories used. Furthermore, the symmetry of production cross sections under time reversal,¹ $\mathfrak{S}_{p'q's't'}^{(pqs't)} = (-1)^{q+q'} \mathfrak{S}_{pqs't}^{(p'q's't')}$, allows the comparison between two cross sections calculated using independent expressions. This symmetry was used as a further indicator of precision.

IV. RESULTS

The calculations of the generalized cross sections were performed on a modern Linux workstation and took about 3 months of CPU time for the CC-pol surface and about 1 month for each of the other three surfaces. The evaluation of the classical trajectories was the most time-consuming part in the computations.

All the calculated transport and relaxation¹ cross sections are characterized by the customary monotonic decrease with temperature, while some of the production cross sections exhibit a maximum at low temperature. The values of the transport and relaxation cross sections are, on average, an order of magnitude larger than that of the production cross sections. The precision of most of the calculated transport and relaxation cross sections is estimated to be better than $\pm 0.3\%$, while the precision of most of the production cross sections is estimated to be better than $\pm 3.0\%$.

Tables of the cross sections employed in this work and

of the calculated transport properties, all evaluated using the CC-pol potential, have been deposited with the Electronic Physics Auxiliary Publication Service.³⁶

A. Shear viscosity

1. Second-order contributions

Using Eq. (1) the viscosity values were calculated from the generalized cross section $\mathfrak{S}(2000)$ combined with the second-order correction factor $f_{\eta}^{(2)}$, evaluated employing expressions given in our previous work.⁷ The calculations indicate that the values of $f_{\eta}^{(2)}$ are close to unity for all temperatures and all potentials considered. The differences between the values of the correction factor calculated using the four potentials studied are small and hence results for only the CC-pol potential are discussed. For this potential $f_{\eta}^{(2)}$ has a value of 1.0055 at 250 K and its magnitude decreases with increasing temperature. At about 1000 K $f_{\eta}^{(2)}$ reaches a minimum of 1.0025 and then increases again with temperature to reach a value of 1.0048 at 2500 K. Overall, the effect of the second-order correction on the viscosity of water is similar to that observed for the other molecules studied so far. The contribution from angular-momentum coupling is very small, at most 0.01%, for all temperatures considered in this work. This contribution is at least an order of magnitude smaller than those observed for the other molecules studied, indicating that the influence of a magnetic field on the viscosity of water vapor is negligible. Hence, our assumption of including only the leading polarization in the description (see the discussion in Ref. 7) is justified.

2. Comparison with experiment

A critical evaluation of viscosity measurements on water, based on data available in 2007, was performed in a joint project between the IAPWS (International Association for the Properties of Water and Steam) and the IATP (International Association for Transport Properties, formerly the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry) and resulted in a “Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance”^{37,38} to be referred to as “the IAPWS 2008 correlation.” This formulation enables the calculation of the viscosity of water for wide ranges of fluid conditions up to 1173 K and 1000 MPa, including the zero-density limit. In 2005 Teske *et al.*³⁹ derived another zero-density viscosity correlation using reliable data sets from the literature and new experimental data at low density, obtained in our laboratory using an all-quartz oscillating-disk viscometer.

As will be shown later in this section, of the four intermolecular potential energy surfaces considered here, the CC-pol surface^{21–23} gives the best agreement with experiment. Accordingly most comparisons for shear viscosity between theory and experiment will be performed using this surface. Figure 1 illustrates the comparison between the values calculated for the CC-pol surface and the two correlations and also with different experimental data. For this comparison we employed the same zero-density viscosity values as Teske *et al.*³⁹ The reader is referred to Refs. 38 and 39 for a com-

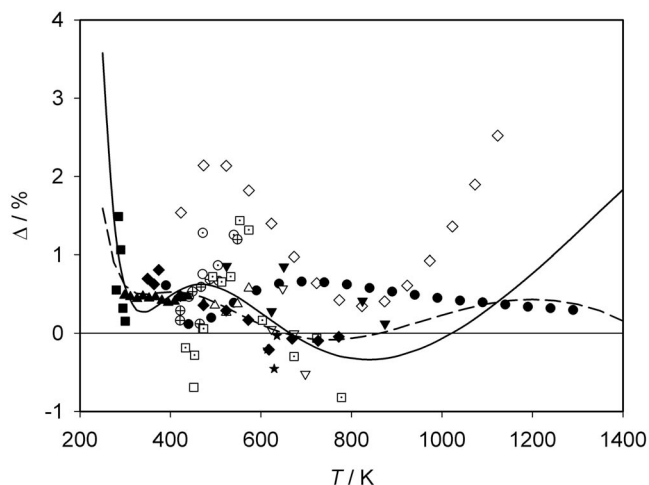


FIG. 1. Deviations of experimental and experimentally based zero-density viscosity coefficients from the values $\eta_{\text{calc-CCpol}}$ calculated for the CC-pol potential of Bukowski *et al.* (Refs. 21–23) for H_2O . Deviations are defined as: $\Delta = (\eta_{\text{exp}} - \eta_{\text{calc-CCpol}}) / \eta_{\text{calc-CCpol}}$. Experimental data: (\diamond) Shifrin (Ref. 40); (\circ) Kestin and Wang (Ref. 41); (\odot) Moszynski (Ref. 42); (\oplus) Kestin and Richardson (Ref. 43); (\bullet) Latto (Ref. 44); (\triangle) Rivkin and Levin (Ref. 45); (∇) Rivkin *et al.* (Ref. 46); (\square) Sato *et al.* (Ref. 47); (\square) Sato *et al.* (Ref. 48); (\blacksquare) Yasumoto (Ref. 49); (\blacklozenge) Timrot *et al.* (Ref. 50); (\blacktriangledown) Nagashima *et al.* (Ref. 51); (\star) Oltermann (Ref. 52); (\blacktriangle) Teske *et al.* (Ref. 39). Experimentally based values: (---) Teske *et al.* (Ref. 39); (—) IAPWS 2008 (Ref. 37).

prehensive account of how the zero-density extrapolation was performed for data of different authors, together with a discussion of the ascribed experimental uncertainties.

Figure 1 shows that in the temperature range from 300 to 1200 K the zero-density viscosity correlations of Teske *et al.*³⁹ and of Huber *et al.*³⁸ (the IAPWS 2008 correlation) are in close agreement with the values calculated for the CC-pol surface.^{21–23} Being based on the same experimental material, the two correlations are generally mutually consistent. However, at high temperatures they extrapolate differently due to the weights chosen for the data of Shifrin⁴⁰ and of Latto⁴⁴ in the fitting procedures used to generate the correlations.

The figure demonstrates that the experimental data of Teske *et al.* in the temperature range of 298–438 K deviate from the calculated values by about +0.5%. In principle, this difference should be decreased by 0.1%–0.2% because Teske *et al.* used an old reference value for the viscosity of argon of Kestin and Leidenfrost⁵³ to calibrate their oscillating-disk viscometer at room temperature. It should be noted that in this temperature range the temperature dependence of these experimental viscosity data is essentially reproduced perfectly by the values calculated using the CC-pol intermolecular potential. The figure reveals further that nearly all experimental data deviate from the calculated values by between -0.5% and $+1.5\%$, apart from the data of Shifrin,⁴⁰ which are characterized by deviations in excess of $+2\%$, not only at very high but also at moderate temperatures around 500 K. In contrast, the experimental data of Latto⁴⁴ are within 1% of the calculated values up to 1350 K.

An essential aspect of the new values calculated with the CC-pol intermolecular potential energy surface^{21–23} is their behavior at low and high temperatures, where experiments are most difficult. As illustrated in Figs. 1 and 2, the devia-

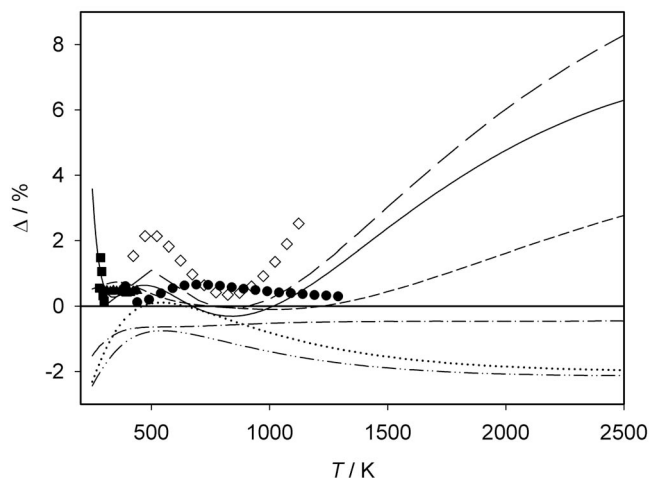


FIG. 2. For H_2O comparison of the extrapolation behavior at low and high temperatures of the values $\eta_{\text{calc-CCpol}}$, calculated for the CC-pol potential of Bukowski *et al.* (Refs. 21–23), with experimental data, experimentally based values considering some input from kinetic theory and simple potential models, calculated values for the other intermolecular potential energy surfaces. Deviations are defined as $\Delta = (\eta_{\text{exp,calc}} - \eta_{\text{calc-CCpol}}) / \eta_{\text{calc-CCpol}}$. Experimental data: (\diamond) Shifrin (Ref. 40); (\bullet) Latto (Ref. 44); (\blacksquare) Yasumoto (Ref. 49); (\blacktriangle) Teske *et al.* (Ref. 39) Experimentally based values: (---), Aleksandrov *et al.* (Ref. 54); (— — —), Fokin and Kalashnikov (Ref. 55); (— — —), IAPWS 2008 (Ref. 37). Theoretically calculated values: (— · — · — ·), SAPT-5s potential of Mas *et al.* (Ref. 16); (····), SAPT-5st potential of Groenboom *et al.* (Ref. 17); (— · — · — ·), SDFT-5s potential of Bukowski *et al.* (Ref. 19).

tions increase rapidly in the low temperature limit. Both correlations in this temperature range rely entirely on the experimental data by Yasumoto.⁴⁹ These data are characterized by relatively large scatter due to the experimental difficulties at the very low water vapor densities. Although in developing the two correlations, Yasumoto's estimated uncertainty of $\pm 0.5\%$ was ascribed to these data, a more realistic estimate appears to be $\pm 1\%$.

Figure 2 illustrates the behavior of the IAPWS 2008 correlation for temperatures up to 2500 K, the temperature considered to be the limit of a physically reasonable extrapolation by the IAPWS.³⁷ The deviations from the calculated values increase with increasing temperature, reaching a maximum of 6% at 2500 K. This is entirely due to the weighting given to the data of Shifrin⁴⁰ in the fitting procedure for the IAPWS correlation.

In addition, it is of interest to compare the calculated values with both a correlation proposed by Aleksandrov *et al.*⁵⁴ and recommended values by Fokin and Kalashnikov.^{55,56} Aleksandrov *et al.* took into account the general behavior as $T \rightarrow 0$ and $T \rightarrow \infty$ of the collision integrals used in kinetic theory for monatomics and determined the parameters in their equation using reliable low-density viscosity data from the literature at temperatures up to 1400 K. Fokin and Kalashnikov⁵⁵ fitted a generalized four-parameter Stockmayer potential to selected experimental viscosity and self-diffusion data of rarefied steam ranging for temperatures between 280 and 1773 K and used the Mason–Monchick^{57,58} approximation to infer values up to 2500 K. In their more recent paper⁵⁶ they used the new experimental data of Ref. 39 at low temperatures to improve their fit slightly but reported viscosity values up to a tem-

perature of 2000 K only. With respect to the high-temperature behavior, we restrict the comparison to the earlier values,⁵⁵ in particular, since the newer values are less than half a percent higher. There exists good agreement between the IAPWS 2008 correlation and the recommended values of Fokin and Kalashnikov,⁵⁵ within their mutual uncertainties. This is not surprising since Fokin and Kalashnikov used a similar data set at high temperatures as the IAPWS 2008 correlation. However, the extrapolation to 2500 K differs significantly from our calculated values. The theoretical basis of the extrapolations of Fokin and Kalashnikov,^{55,56} as well as that of Aleksandrov *et al.*,⁵⁴ is much less well founded than the methods employed here. In particular, the Fokin and Kalashnikov^{55,56} extrapolation relies on the unrealistic model potential where the softness of the repulsive wall is determined by a single empirical parameter that is sensitive to the high temperature data used in its determination.

Figure 2 also compares the values calculated for the CC-pol intermolecular potential energy hypersurface^{21–23} with those computed using the other potential surfaces being considered here.^{16,17,19} Taking into account the agreement with the experimental data, CC-pol proves to be the best of these surfaces. With differences of no more than 2% at most between the results using all four surfaces, this level of agreement is very encouraging. In particular, the SDFT-5s potential,¹⁹ based on a very different theoretical approach to that used for CC-pol, yields viscosities which are only slightly smaller than those obtained with the CC-pol surface for temperatures above 500 K. The older SAPT-5s (Ref. 16) and SAPT-5st (Ref. 17) potentials show somewhat larger deviations, especially at higher temperatures, indicating that they are, on average, too repulsive.

We consider that the present calculations provide the best estimate of the viscosity of water at temperatures down to 250 K. Noting the excellent agreement with our computed values of the temperature dependence of the experimental data by Teske *et al.*³⁹ between 298 and 438 K, and also of the consistency with the experimental data by Latto⁴⁴ up to 1350 K, we expect that our calculations provide the most reliable results in the temperature range up to 2500 K, previously covered by extrapolations. We estimate the accuracy of the computed values to be of the order of $\pm 1\%$ at 250 and 2500 K and even better at intermediate temperatures.

B. Self-diffusion

In contrast to the situation for the shear viscosity and thermal conductivity, (see Sec. IV C 3), there are very few measurements of self-diffusion in low-density water vapor. We are aware of only two: a relatively old measurement by Swinton⁵⁹ in 1971 of the diffusion of tritiated water, HTO, in H_2O and a more recent measurement in 2006 using the NMR spin-echo method by Yoshida *et al.*^{60,61}

Swinton⁵⁹ measured self-diffusion at five temperatures between 363 and 517 K with pressures of 0.01–0.3 bar. The precision of his results ranged from $\pm 1.5\%$ at 363 K to $\pm 4\%$ at 517 K. There was no discussion of any pressure dependence of the diffusion coefficients. We have assumed that the

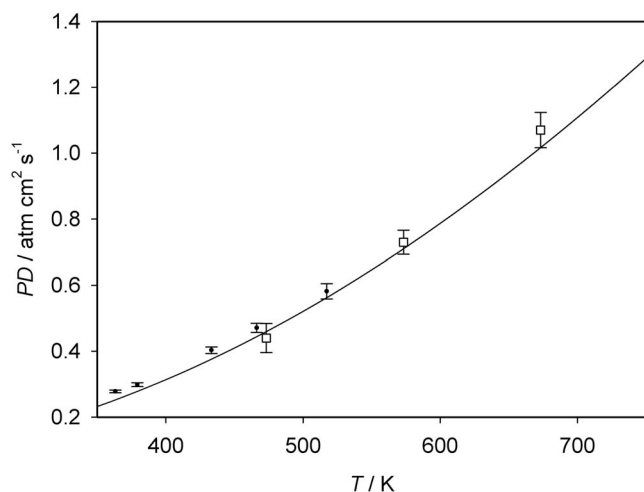


FIG. 3. Comparison of measured and calculated values of the diffusion coefficient at one atmosphere (PD) for H_2O . Experimental data: (●) Swinton (Ref. 59); (□) Yoshida *et al.* (Refs. 60 and 61). The error bars shown correspond to the estimated experimental uncertainties (see text). The uncertainties for the three intermediate temperatures of Swinton (Ref. 59) have been loosely interpolated between the values at 363 and 517 K. Calculated values: (—) CC-pol potential surface of Bukowski *et al.* (Refs. 21–23).

tabulated values are reduced to a pressure of 1 atm. When comparing with calculated values we have scaled these measured values by the usual factor to allow for the different reduced masses of $HTO-H_2O$ and H_2O-H_2O collisions. This factor would be exact for systems described classically by a spherically symmetric potential common to both isotopomers.

The spin-echo measurements^{60,61} were taken at 473, 573, and 673 K and the results at the two higher temperatures were extrapolated to the zero-density limit. However, measurements at just two pressures were available at 473 K and the value at the lower density (0.0041 g cm^{-3}) was taken as the zero-density limit.^{60,61} The uncertainty of the measurements is listed as $\pm 5\%$. When Fokin and Kalashnikov⁵⁶ employed these results, they assigned an uncertainty of $\pm 10\%$ to the 473 K diffusion coefficient and $\pm 5\%$ to the values at the other two temperatures, and we have adopted these uncertainties.

Both these sets of results are compared in Fig. 3 with the calculated values using the CC-pol potential surface. Neglecting the temperature difference between the Swinton⁵⁹ result at 466.2 K and the Yoshida *et al.*⁶¹ result at 473.2 K, these two measurements by quite different techniques are seen to be mutually consistent. Our calculated values are smaller than the measured values of Swinton⁵⁹ with the difference falling from 10% at 363 K to 3% at 517 K. These differences are significantly larger than the estimated experimental uncertainty, except at the highest temperature. Given the possible effect on the measured values of the reduction to zero density, it is difficult to assess the significance of these differences at the lower temperatures. The three spin-echo measurements^{60,61} are all consistent with theory within the estimated experimental uncertainty.

The differences between the values calculated using the four surfaces considered here are less than 1.5% at all tem-

peratures considered, with the CC-pol results almost always the largest. As the differences are very similar to those in Fig. 2 for shear viscosity they are not shown.

Matsunaga and Nagashima⁶² have estimated the self-diffusion coefficient of water vapor in the dilute-gas limit for temperatures between 273 and 2000 K, based on values calculated for a spherical potential whose parameters were chosen to yield agreement with the shear viscosity measurements. They estimated the accuracy of their results as $\pm(6-8)\%$. Comparison with values calculated using the CC-pol potential shows agreement within $\pm 2\%$ for temperatures in the range of 500–2000 K. The largest difference, +13%, occurred at 273 K but the difference fell rapidly with increasing temperature to about 5% at 350 K and 2% at 500 K.

Fokin and Kalashnikov⁵⁶ have also estimated values of the self-diffusion coefficient based on a nonspherical potential and the Mason–Monchick^{57,58} approximation, as discussed previously (see Sec. IV A 2). The values of Fokin and Kalashnikov⁵⁶ lie between 3% above and 5% below our calculated values, consistent with their estimate of the uncertainty of their results as 6%–8%. While the largest deviations of the results of Ref. 56 for shear viscosity and self-diffusion from our calculated values are comparable, their temperature dependence is rather different.

C. Thermal conductivity

1. Vibrational degrees of freedom

All the cross sections in this work have been calculated assuming that the water molecules can be represented as rigid rotors (rr) in their ground vibrational state (00). However, calculation of the thermal conductivity requires knowledge of cross sections that take into account both rotational and vibrational degrees of freedom, as energy stored in the vibrational degrees of freedom will influence the transport of energy through the gas. To account for the presence of the vibrational degrees of freedom in a water molecule, we have corrected, using the methodology and notation described in Ref. 8, all the cross sections $\mathfrak{S}_{p'q's't'}^{pqs't}(\kappa)$ with $t+t' > 0$ which enter the description of thermal conductivity. In line with our previous work, we use the subscript “int” to show that the particular generalized cross section has been corrected. The correction is based on the assumption that the vibrational energy is “frozen” during the collision and that the vibrational states of the molecules will have negligible influence on the differential cross section for the scattering of two rotationally active molecules.

In the first-order approximation for thermal conductivity, $n=1$ in Eq. (3), two cross sections, $\mathfrak{S}_{1001}^{(1010)}$ and $\mathfrak{S}(1001)$, require correction. The correction for the production cross section $\mathfrak{S}_{1001}^{(1010)}_{\text{int}}$ is the larger of the two and exhibits a strong temperature dependence, as already noted for carbon dioxide and methane. The ratio $\mathfrak{S}_{1001}^{(1010)}_{\text{int}}/\mathfrak{S}_{1001}^{(1010)}_{\text{rr00}}$ is near unity at 300 K, but decreases to 0.78 at 1000 K and 0.64 at 2000 K. However, similarly to methane at high temperatures, this production cross section is approximately 20 times smaller than the two transport cross sections, and hence its contribution to the thermal conductivity is small.

For $\mathcal{S}(1001)_{\text{int}}$ it can be shown⁸ that the correction is of the form

$$\mathcal{S}(1001)_{\text{int}} = \left(\frac{c_{\text{rot}}}{c_{\text{int}}} \right) \mathcal{S}(1001)_{\text{rr00}} + \left(\frac{c_{\text{vib}}}{c_{\text{int}}} \right) \mathcal{S}'(1000)_{\text{rr00}}. \quad (7)$$

Rotational relaxation of water molecules is relatively slow (our calculations yield a rotational collision number $\zeta_{\text{rot}}=5-12$ for temperatures between 300 and 2000 K), so one would expect that, on average, rotational energy is primarily transported by the translational motion of the molecules. Hence, one would expect the value of $\mathcal{S}(1001)_{\text{rr00}}$ to be approximately equal to that of $\mathcal{S}'(1000)_{\text{rr00}}$. This behavior was certainly observed for methane where the rotational relaxation number is comparable with that of water. However, our calculations indicate that the ratio $\mathcal{S}'(1000)_{\text{rr00}}/\mathcal{S}(1001)_{\text{rr00}}$ lies between 0.38 and 0.54 over the temperature range considered. This clearly indicates that in strongly polar molecules, such as water, rotationally resonant collisions play an important part, as has been anticipated by Ref. 58. Such collisions nearly double the value of $\mathcal{S}(1001)_{\text{rr00}}$ cross sections. As a result of these rotationally resonant collisions, the correction for $\mathcal{S}(1001)_{\text{int}}$ is much larger than in previous studies and the ratio $\mathcal{S}(1001)_{\text{int}}/\mathcal{S}(1001)_{\text{rr00}}$ falls off from near unity at 300 K to 0.7 at 2000 K. The behavior of the magnitude of this ratio resembles more that of a very much more rotationally active molecule, such as carbon dioxide, than it does the behavior of the rotationally similar methane molecule.

The overall effect on the thermal conductivity of correcting the cross sections for the vibrational degrees of freedom is strongly dependent on temperature. Although the effect is small at 300 K, of the order of 0.3%, at 1000 K it increases to 8.6%, and at 2000 K it reaches 16.6%. For comparison, the correction at 1000 K for carbon dioxide amounted to approximately 5%. The smallness of the effect for carbon dioxide is due to the much larger contribution of the production cross section $\mathcal{S}_{1001}^{(1010)}_{\text{int}}$, which largely canceled the effect of correcting $\mathcal{S}(1001)_{\text{rr00}}$.

In the full second-order approximation (see below), the effect of this vibrational correction on the thermal conductivity coefficient is very similar: at 1000 K the overall effect on the thermal conductivity is 8.4%, while at 2000 K it is 15.8%.

2. Second-order contributions

The values of thermal conductivity were calculated in the second-order approximation from the generalized cross sections using Eq. (3), where the second-order correction factor $f_{\lambda}^{(2)}$ has been calculated by means of expressions given in our previous work.⁸ Similarly to the viscosity, the value of the correction factor is close to unity for all the temperatures and all the potentials considered. Furthermore, the value of $f_{\lambda}^{(2)}$ exhibits a similar temperature dependence to that observed for $f_{\eta}^{(2)}$ and is also very weakly dependent on the intermolecular potential. At the lowest temperature (250 K) considered in this work, the magnitude of $f_{\lambda}^{(2)}$ for CC-pol is 1.009. The correction factor initially decreases with increas-

ing temperature, reaching a minimum of 1.0076 at about 400 K, followed by an increase to 1.027 at 2500 K. The contribution from angular-momentum coupling is again very small for all temperatures considered, increasing from about 0.01% at 250 K to 0.26% at 2500 K.

3. Comparison with experiment

The ‘‘Revised Release on the IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance,’’ issued in 1998 and to be referred to as ‘‘the Revised IAPS 1998 correlation,’’⁶³ is the latest and most accurate correlation proposed for the thermal conductivity of water, based on the critical assessment of experimental measurements. The low-density thermal conductivity values of this correlation are characterized by uncertainties of $\pm 2\%$ at temperatures below about 850 K and of $\pm 3\%$ at higher ones. For the comparison with our calculated values at zero density, we have selected the experimental values of Refs. 64–81, proposed by a Special Committee of IAPS as primary data sets.⁸² Additional suitable experimental data of Refs. 83–91, of comparable accuracy, taken from the open literature or from the data bank by Assael *et al.*⁹² were also selected. In order to obtain the experimental value of thermal conductivity at zero density either isothermal values as a function of density were extrapolated to this limit or individual values at low density were corrected to it using the density dependence of the Revised IAPS 1998 correlation.⁶³

The hot-wire (HW) method,^{64–69,71,73,80,83,84,89,91} the concentric-cylinder (CC) method,^{68,70,72,74–79,81,85,87,90,93} the parallel-plate method,^{86,88} and the transient HW (THW) technique⁹⁴ were employed in performing the measurements on water vapor and steam. In principle, the uncertainties achieved with these experimental techniques decrease along this series of methods towards the THW method. However, in the case of water vapor and steam, the situation is complicated, since the temperatures required were often very high so that numerous difficulties limited the accuracy of the experiments. In particular, convection, radiative heat transfer, parasitic heat transfer via the ends of the measuring device, temperature jumps at the solid-fluid boundaries, especially at low fluid density, contamination of the solid surfaces during the experiment, and irregularities in the idealized temperature profile required for the application of the working equations were cited as possible causes of lower accuracy.

Figures 4 and 5 illustrate the deviations of experimental data for the thermal conductivity in the limit of zero density from our calculations based on the CC-pol potential of Bukowski *et al.*^{21–23} For clarity, because of the quantity of available data, the earlier data are presented in Fig. 4 and the later in Fig. 5. The best data of the selected measurements still show a scatter of the order of $\pm 2\%$ at most temperatures. But there exist larger differences between the measurements of different workers. Notwithstanding this observation, it is also clear that there is a systematic trend of the calculated values progressively underestimating the experimental data as the temperature increases.

This trend is confirmed in both figures where the calculations are compared with the thermal conductivity in the limit of zero density based on the Revised IAPS 1998

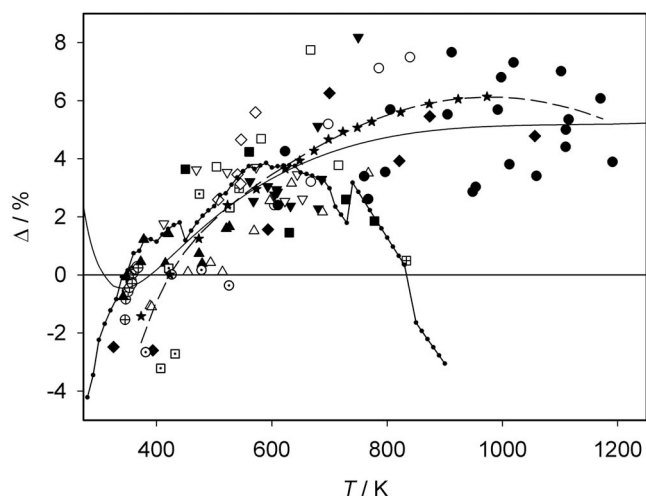


FIG. 4. Deviations of experimental and experimentally based zero-density thermal conductivity coefficients from the calculated values $\lambda_{\text{calc-CCpol}}$ for the CC-pol potential of Bukowski *et al.* (Refs. 21–23) for H_2O . Deviations are defined as $\Delta = (\lambda_{\text{exp}} - \lambda_{\text{calc-CCpol}}) / \lambda_{\text{calc-CCpol}}$. Experimental data: (\oplus) Milvertton (Ref. 64); (\blacktriangle) Timrot and Vargaftik (Ref. 65); (\blacktriangledown) Vargaftik (Ref. 66); (\blacklozenge) Vargaftik and Oleshchuk (Ref. 67); (\square) Vargaftik and Smirnova (CC method) (Ref. 68); (\blacksquare) Vargaftik and Smirnova (HW method) (Ref. 68); (\circ) Vargaftik and Tarzimanov (Ref. 69); (\boxplus) Vines (Ref. 70); (\diamond) Tarzimanov (Ref. 71); (\triangle) Vargaftik and Zaitseva (at 0.5 bar) (Ref. 83); (∇) Keyes and Vines (Ref. 72); (\bullet) Vargaftik and Zimina (Ref. 73); (\odot) Baker and Brokaw (Ref. 84); (\square) Venart (Ref. 74). Experimentally based values: (---), Vargaftik and Zimina (Ref. 73); (*), IAPS Skeleton Tables 1964 (Refs. 95 and 96); (—•—•—), Standard Reference Values of Powell *et al.* (Ref. 97); (—), Revised IAPS 1998 correlation (Ref. 63).

correlation.⁶³ It is obvious that from 400 to 1100 K the difference between the values using this correlation and the values for the CC-pol potential increases continuously up to more than +5%. Further the extrapolation behavior at low temperatures down to 273 K differs markedly. Although the differences at higher temperatures are just outside the mutual uncertainties of the experimentally based correlation ($\pm 3\%$) and of the theoretical calculation ($\pm 1\%$), it is the temperature dependence of the Revised IAPS 1998 correlation that is not reproduced by the calculations.

The pre-1965 experiments mostly measured near to atmospheric pressure: the experimentally based correlation of Vargaftik and Zimina,⁷³ the IAPS Skeleton Tables from 1964,^{95,96} and standard reference values of Powell *et al.*,⁹⁷ all reported for atmospheric pressure, are compared, after correction to zero density, in Fig. 4. It should be mentioned that Vargaftik and Zimina developed their correlation including the experimental data of Refs. 66–68, 70, 72, and 73, with a correction to the data point at 833 K of Vines⁷⁰ for a possible temperature-jump effect. This correction is the reason for the large difference between the correlation by Vargaftik and Zimina and the standard reference values of Powell *et al.*⁹⁷ at high temperatures. The figure makes evident that the correlated values by Vargaftik and Zimina establish the basis for the IAPS Skeleton Tables from 1964 and for the later Revised IAPS 1998 correlation.

The experiments performed between 1967 and 1989 are compared with our calculations in Fig. 5. These experiments were mostly directed to the determination of the density dependence of the thermal conductivity and to its critical en-

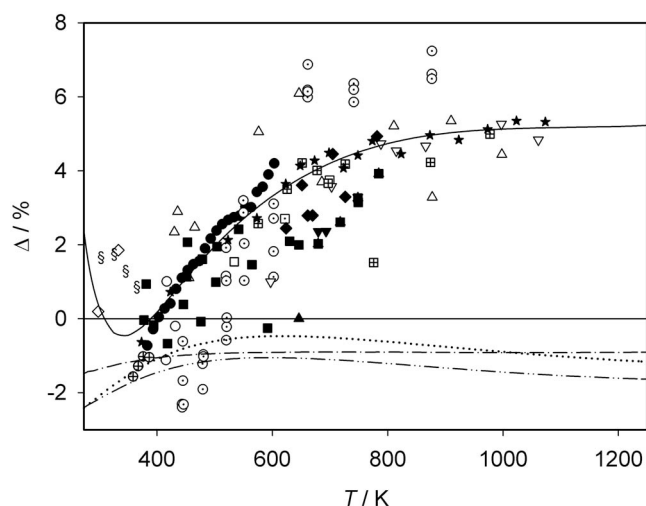


FIG. 5. Deviations of experimental data, of experimentally based values, and of calculated values for different intermolecular potential energy surfaces from the zero-density thermal conductivity coefficients $\lambda_{\text{calc-CCpol}}$ calculated for the CC-pol potential of Bukowski *et al.* (Refs. 21–23) for H_2O . Deviations are defined as $\Delta = (\lambda_{\text{exp,calc}} - \lambda_{\text{calc-CCpol}}) / \lambda_{\text{calc-CCpol}}$. Experimental data: (\circ) Brain (Ref. 75); (\bullet) Bury *et al.* (Ref. 76); (\odot) Brain (Ref. 77); (\diamond) Dijkema *et al.* (Ref. 85); (\blacktriangle) Le Neindre *et al.* (Ref. 78); (\square) Tarzimanov and Zainullin (Ref. 79); (\triangle) Vargaftik *et al.* (Ref. 80); (\blacksquare) Bury *et al.* (Ref. 81); (\square) Sirota *et al.* (Refs. 86 and 88); (∇) Popov and Dulnev (Ref. 87); (\oplus) Curtiss *et al.* (Ref. 89); (\blacktriangledown) Tufeu and Le Neindre (Ref. 90); (\S) Miroshnichenko and Makhrov (Ref. 91); (\blacklozenge) Tufeu and Le Neindre (Ref. 93); (\boxplus) Tarzimanov and Gabitov (Ref. 94). Experimentally based values: (*), IAPS Skeleton Tables 1977 (Refs. 82, 98, and 99); (—), Revised IAPS 1998 correlation (Ref. 63). Calculated values: (---), SAPT-5s potential of Mas *et al.* (Ref. 16); (---), SDFT-5s potential of Bukowski *et al.* (Ref. 19).

hancement. In terms of zero-density thermal conductivity extracted from these measurements, the somewhat more recent experiments by a French group^{78,81,90,93} tend to support lower values, whereas the newer Russian papers confirm consistently the older ones, which formed the basis of the original correlation by Vargaftik and Zimina.⁷³

Not all of these measurements are independent, however. Those of Bury *et al.*⁷⁶ were adjusted to the IAPS Skeleton Tables from 1964 at atmospheric pressure, as reported by Grigull.¹⁰⁰ For the evaluation of the measurements with their parallel-plate apparatus, Sirota *et al.*^{86,88} changed the value of the emissivity coefficient of the stainless-steel plates from 0.48 given in their earlier paper¹⁰¹ to 0.32, resulting in a thermal conductivity value at atmospheric pressure close to the correlation by Vargaftik and Zimina.⁷³ Nonetheless, there is overwhelming experimental support for the temperature dependence of the Revised IAPS 1998 correlation.

At this stage it is not clear why the current calculations cannot reproduce this temperature dependence, especially as the CC-pol potential reproduces very accurate viscosity data (see Sec. IV A 2). Nevertheless, the results using the CC-pol potential are, at temperatures below 500 K, within 2% of the Revised IAPS 1998 correlation.

We suggest that further discussion of the differences between the experimental data and the calculated values needs to focus primarily on the HW method with which most of the early experiments included in the correlation of Vargaftik and Zimina⁷³ were performed. The urgency for new and ac-

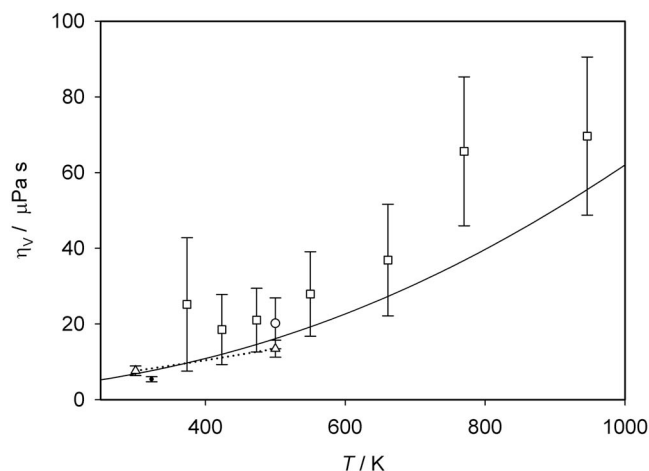


FIG. 6. Comparison of measured and calculated values of the volume viscosity η_v for H_2O . Experimental data: (●) Roesler and Salm (Ref. 102); (□) Bass *et al.* (Ref. 103); (○) Keaton and Bass (Ref. 104); (Δ ···· Δ) Synofzik *et al.* (Ref. 105). The error bars shown correspond to the estimated experimental uncertainties (see text). Second-order calculations: (—) CC-pol potential surface of Bukowski *et al.* (Refs. 21–23).

curate measurements above 1000 K, already stressed by Fokin and Kalashnikov,⁵⁶ is also strongly supported.

The comparison between the different values calculated for the CC-pol intermolecular potential energy surface^{21–23} and for the other potential surfaces^{16,17,19} is also shown in Fig. 5. The agreement among the potentials is similar to that observed for viscosity. The other potentials considered here give results differing even more from the Revised IAPS 1998 correlation at high temperatures.

D. Volume viscosity

Results for the volume viscosity were calculated for the four potential energy surfaces of interest. For the CC-pol surface the difference between the first-order and second-order results increased slowly with increasing temperature but never exceeded 3% for temperatures between 250 and 2500 K. The results in second order using the four surfaces involved never differed from the CC-pol values by more than 1.5%.

Four sets of measurements in water vapor of rotational collision numbers or relaxation times or rates are available: one at 323.15 K by Roesler and Salm,¹⁰² with a quoted uncertainty of $\pm 25\%$, one by Bass *et al.*¹⁰³ covering the temperature range from 373 to 946 K with uncertainties falling from $\pm 70\%$ at 373 K to $\pm 30\%$ at 946 K, a measurement at 500 K with an uncertainty of $\pm 33\%$ by Keaton and Bass,¹⁰⁴ and measurements between 300 and 500 K with uncertainties of about $\pm 20\%$ by Synofzik *et al.*¹⁰⁵ All four papers mentioned the difficulty of these measurements. The results have been converted to volume-viscosity values using Eq. (6). Comparison is made in Fig. 6 with results obtained in second order using the CC-pol surface. It can be seen that almost all the measurements are consistent with the calculated values, and for those for which the calculated value lies outside the error bars, the difference is less than twice the listed experimental uncertainty.

While the accuracy of these measurements does not allow a stringent test of the potential surface employed, for the properties considered here, the volume viscosity is the one most sensitive to the anisotropy of the surface.

V. SUMMARY AND CONCLUSIONS

We have calculated the shear viscosity, thermal conductivity, self-diffusion, and volume viscosity of low-density water vapor over the temperature range of 250–2500 K. The generalized cross sections required in the best available kinetic theory were computed by means of the classical-trajectory method employing four different rigid-rotor water-water intermolecular potential energy hypersurfaces.

For the viscosity, very good agreement with the best experimental data is obtained when using the CC-pol potential of Bukowski *et al.*^{21–23} The data of Teske *et al.*,³⁹ which are the most accurate at low temperatures, differ from the values calculated using the CC-pol surface by only about +0.5%. The high-temperature data of Latto,⁴⁴ which extend up to 1350 K, show also similar small deviations. The IAPWS 2008 correlation³⁷ shows relatively large deviations from the calculated values at very high, and particularly very low, temperatures. The calculated values are expected to be more accurate than the IAPWS 2008 correlation at such temperatures. We estimate the uncertainties of the computed values to be about $\pm 1\%$ at 250 K and 2500 K, and even better at intermediate temperatures.

Differences between theory and experiment for self-diffusion were found to be consistent with the experimental uncertainties for the more recent NMR spin-echo measurements.^{60,61} However, at all but the highest temperature available (517 K), the differences with the HTO– H_2O diffusion measurements⁵⁹ were significantly larger than the estimated experimental precision. No reduction to the zero-density limit was performed for these observations.

For the thermal conductivity the deviations between most of the experimental data and the values calculated with the four potential energy surfaces are comparably small at low temperatures, but increase with higher temperatures to about +5% compared with calculated values using the CC-pol surface. Considering the very good agreement between theory and experiment in the case of viscosity, it seems unlikely, but not impossible, that the calculated values for the thermal conductivity are characterized by such large uncertainties. These differences need further investigation of both possible deficiencies of the theory, especially for strongly polar molecules, and also of all the corrections used for the evaluation of the thermal conductivity measurements, particularly with the HW method. Further measurements above 1000 K are highly desirable.

In the case of the volume viscosity, where experiments are especially difficult, theory and experiment^{102–105} were generally consistent within the rather large uncertainty of most of the measurements.

While differences between the results using the four potential energy surfaces considered^{16–23} were small, the CC-pol surface^{21–23} gave the best overall agreement with the measurements.

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