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RESEARCH ARTICLE

An improved kinetic theory approach for calculating the thermal conductivity of polyatomic gases

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A new kinetic theory approach for calculating the thermal conductivity of a dilute polyatomic gas from the intermolecular pair potential is presented. The contributions due to internal degrees of freedom have been separated into a classical rotational and a quantum-mechanical vibrational part. Assuming that the vibrational states of the molecules do not significantly influence the collision trajectories, and that vibrationally inelastic and vibrationally resonant collisions are rare, we have obtained a simple self-diffusion mechanism for the vibrational contribution to the thermal conductivity. For non-polar gases like methane or nitrogen, the new approach yields thermal conductivity values that are very close to those obtained with the previously used kinetic theory approach. However, for polar gases like hydrogen sulphide and water vapour, the values obtained with the new scheme are much closer to the most accurate experimental data.

Keywords: kinetic theory; thermal conductivity; self-diffusion coefficient; hydrogen sulphide; water vapour

1. Introduction

The relationship between the shear viscosity η and the thermal conductivity λ of a dilute monatomic gas, $\lambda/\eta = f c_V$, has already been found empirically by Maxwell. Here, $c_V = c_{V,\text{tr}} = 3R/2M$ is the specific heat capacity at constant volume and $f = 5/2$. For such a gas, the heat transport in a temperature gradient is determined by binary collisions, in which translational energy is exchanged between the particles. Using the kinetic theory of gases, Chapman [1] showed that binary collisions equally influence viscosity and thermal conductivity, and that $f = 5/2$.

For polyatomic gases, where $c_V = c_{V,\text{tr}} + c_{\text{int}} = c_{V,\text{tr}} + c_{\text{rot}} + c_{\text{vib}}$ (contributions due to electronic excitations can usually be neglected), experimental data for η and λ showed that $f < 5/2$ [2]. The dynamics of collisions between polyatomic molecules is far more complex than in the monatomic case due to the anisotropic intermolecular potential. Not only translational energy is exchanged during collisions, but also internal energy. There is no simple kinetic theory relation for determining the value of f .

As an empirical improvement, Eucken [3] suggested to decompose the thermal conductivity into two or three independent parts,

$$\lambda = \lambda_{\text{tr}} + \lambda_{\text{int}} = \lambda_{\text{tr}} + \lambda_{\text{rot}} + \lambda_{\text{vib}}, \quad (1)$$

where the individual contributions are given by $\lambda_{\text{tr}} = \eta f_{\text{tr}} c_{V,\text{tr}}$ with $f_{\text{tr}} = 5/2$, $\lambda_{\text{int}} = \eta f_{\text{int}} c_{\text{int}}$ with $f_{\text{int}} = 1$, $\lambda_{\text{rot}} = \eta f_{\text{rot}} c_{\text{rot}}$ with $f_{\text{rot}} = 1$ and $\lambda_{\text{vib}} = \eta f_{\text{vib}} c_{\text{vib}}$ with $f_{\text{vib}} = 1$.

The Eucken formula led to an improved description of experimental data, but the agreement was not satisfactory over an extended temperature range. It was assumed that f_{int} is temperature dependent [4], with experimental data indicating $0.7 < f_{\text{int}} < 1.3$ [4].

Chapman and Cowling [5] as well as Schäfer [6] proposed a modified Eucken formula. They assumed a diffusion mechanism for internal energy transport with $f_{\text{int}} = \mathcal{D}_{\text{int}}/\eta$, where $\mathcal{D}_{\text{int}} = \rho D_{\text{int}}$ is a density-independent diffusion coefficient for internal energy. Thus,

$$\lambda = \lambda_{\text{tr}} + \mathcal{D}_{\text{int}} c_{\text{int}} = \lambda_{\text{tr}} + \mathcal{D}_{\text{rot}} c_{\text{rot}} + \mathcal{D}_{\text{vib}} c_{\text{vib}}. \quad (2)$$

To a first-order approximation, this expression could be justified theoretically [4,7,8], but did not result in a significant improvement since the quantities \mathcal{D}_{int} , \mathcal{D}_{rot} and \mathcal{D}_{vib} were unknown and were usually replaced by the self-diffusion coefficient, $\mathcal{D}_{\text{self}} = \rho D_{\text{self}}$.

In 1962, Mason and Monchick [4] showed, based on the then available kinetic theories for polyatomic gases of Wang Chang and Uhlenbeck [9,10] (semi-classical) and of Taxman [11] (classical), that there is a coupling between λ_{tr} and λ_{int} due to inelastic collisions, resulting in a decrease of λ_{tr} and an increase of λ_{int} . At that time, the generalised cross sections contributing to the thermal conductivity could not yet be computed. Therefore, these cross sections were approximated [4,12] using collision integrals for spherical particles, diffusion coefficients for internal energies (\mathcal{D}_{rot} , \mathcal{D}_{vib}) and collision numbers (Z_{rot} , Z_{vib}) or relaxation times

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(τ_{rot} , τ_{vib}) for energy exchange between translational and internal degrees of freedom. Some of these quantities were accessible from experiments. However, attempts to fit the unknown quantities and their temperature dependence to experimental data for the thermal conductivity were only moderately successful [13–15].

Today, highly accurate *ab initio* pair potentials and efficient classical trajectory (CT) codes for calculating generalised cross sections for rigid molecules of arbitrary structure are available [16,17]. For the calculation of the thermal conductivity, Bich and co-workers [18,19] developed a scheme based on the kinetic theory of Wang Chang and Uhlenbeck [9,10] to correct the rigid-rotor cross sections for the effects of vibrational energy transport. For carbon dioxide [19], methane [20], hydrogen sulphide [21,22] and nitrogen [23], this procedure resulted in satisfactory agreement between theoretically calculated thermal conductivity values and the most accurate experimental data. For water vapour [24], the agreement with experimental data was only satisfactory for temperatures up to about 500 K, where the vibrational degrees of freedom are not significantly excited. At higher temperatures, the calculated values systematically deviate from the experimental data. At 1000 K, average deviations of about -5% were observed.

In this paper, we present an improved approach to correct thermal conductivity values obtained from CT calculations with rigid rotors for the effects of vibrational energy transport. We have tested the new approach by calculating the thermal conductivities of CH₄, N₂, CO₂, H₂S and H₂O in the dilute-gas limit.

2. Formal kinetic theory for the thermal conductivity of molecular gases

The transport properties of a dilute molecular gas can be obtained from the first-order approximation of the generalised Boltzmann equation [25]. In this approximation, it is assumed that the gas is not too far from thermodynamic equilibrium, and that only binary collisions occur. The one-particle distribution function can then be written as

$$f = f^{(0)}(1 + \phi), \quad (3)$$

where $f^{(0)}$ is the one-particle distribution function for the local equilibrium,

$$f^{(0)}(\mathbf{r}, t) = \frac{n(\mathbf{r}, t)}{Z_{\text{int}}} \left(\frac{m}{2\pi k_{\text{B}} T(\mathbf{r}, t)} \right)^{3/2} \times \exp[-(W^2 + \mathcal{E}_{\text{int}})], \quad (4)$$

$$\mathbf{W} = \left(\frac{m}{2k_{\text{B}} T} \right)^{1/2} \mathbf{C}, \quad \mathcal{E}_{\text{int}} = \frac{E_{\text{int}}}{k_{\text{B}} T},$$

and ϕ is a perturbation function, $\phi \ll 1$. With this ansatz, we obtain the linearised Boltzmann equation [25],

$$\frac{\partial \ln f^{(0)}}{\partial t} + \mathbf{c} \cdot \nabla \ln f^{(0)} = -\mathcal{R}\phi. \quad (5)$$

In the above equations, n is the number density, m is the molecular mass, Z_{int} is the partition function for the internal degrees of freedom, \mathbf{c} is the particle velocity, \mathbf{C} is the particle velocity relative to the centre-of-mass velocity of the volume element, \mathbf{W} is the reduced particle velocity, \mathcal{E}_{int} is the reduced internal energy and \mathcal{R} is the linearised collision operator. The time derivative in Equation (5) can be eliminated using conservation equations from the zeroth-order solution of the Boltzmann equation and we obtain [25]

$$\frac{\partial \ln f^{(0)}}{\partial t} + \mathbf{c} \cdot \nabla \ln f^{(0)} = \sum_{\alpha} \Psi^{\alpha} \odot \mathbf{X}^{\alpha} = -\mathcal{R}\phi, \quad (6)$$

where Ψ^{α} is a microscopic flux and \mathbf{X}^{α} is the respective thermodynamic force. For the thermal conductivity, we only need to consider the energy flux Ψ^E , which is caused by a temperature gradient $\mathbf{X}^E = \nabla \ln T$:

$$-\mathcal{R}\phi = \Psi^E \cdot \mathbf{X}^E. \quad (7)$$

The perturbation function ϕ is expanded in terms of an orthonormal set of basis tensors Φ_k^{pqrst} [25,26] (if $p = 0$ or $q = 0$, the tensor rank k is unique and can be omitted) with expansion coefficients X^{pqrst} ,

$$\phi = -\frac{1}{n} \sum_{qrst} \Phi_1^{1qrst} X^{1qrst} \cdot \mathbf{X}^E, \quad (8)$$

so that

$$\frac{1}{n} \sum_{qrst} \mathcal{R} \Phi_1^{1qrst} X^{1qrst} \cdot \mathbf{X}^E = \Psi^E \cdot \mathbf{X}^E. \quad (9)$$

After multiplying with the basis vector Φ_1^{1qrst} , we can take the equilibrium average and obtain a system of linear equations for the coefficients $X^{1q's't'}$,

$$\frac{1}{n} \sum_{q's't'} \left\langle \Phi_1^{1qrst} \middle| \mathcal{R} \Phi_1^{1q's't'} \right\rangle_0 X^{1q's't'} \cdot \mathbf{X}^E = \left\langle \Phi_1^{1qrst} \middle| \Psi^E \right\rangle_0 \cdot \mathbf{X}^E. \quad (10)$$

The basis vectors Φ_1^{1qrst} can be written as

$$\Phi_1^{1qrst} = N_{qrst} [\overline{\mathbf{W}\mathbf{j}^q}]_1 L_s^{(3/2)}(W^2) R_t^{(q)}(\mathcal{E}_{\text{int}}), \quad (11)$$

where $\overline{\mathbf{j}^q}$ is a traceless q -fold tensor product of the reduced angular momentum vector \mathbf{j} with itself, $[\dots]_k$ denotes a contraction (explained in Ref. [27]), $L_s^{(3/2)}(W^2)$

is an associated Laguerre polynomial and $R_r^{(q)}(\mathcal{E}_{\text{int}})$ is a Wang Chang–Uhlenbeck polynomial [9,10,26]. The classical limit of $R_r^{(q)}(\mathcal{E}_{\text{int}})$ for a rigid rotor is $L_r^{(q)}(\mathcal{E}_{\text{rot}})$ for a linear rotor [28] and $L_r^{(q+1/2)}(\mathcal{E}_{\text{rot}})$ for a non-linear rotor [17]. The normalisation constant N_{qst} is chosen so that

$$\langle \Phi_1^{1qst} | \Phi_1^{1q's't'} \rangle_0 = \delta_{qq'} \delta_{ss'} \delta_{tt'} \Delta^{(1)}, \quad (12)$$

where $\Delta^{(1)}$ is the isotropic projection tensor of rank two [27]. The microscopic energy flux Ψ^E can be expressed in terms of Φ^{1010} and Φ^{1001} as a sum of two contributions,

$$\Psi^E = \Psi_{\text{tr}}^E + \Psi_{\text{int}}^E = C^{1010} \Phi^{1010} + C^{1001} \Phi^{1001}, \quad (13)$$

where $C^{1010} = (5k_B T/2m)^{1/2}$ and $C^{1001} = (c_{\text{int}} T)^{1/2} = (C_{\text{int}} T/m)^{1/2}$. The expression $\langle \Phi_1^{1qst} | \mathcal{R} \Phi_1^{1q's't'} \rangle_0$ in Equation (10) can be written as [25]

$$\begin{aligned} & \langle \Phi_1^{1qst} | \mathcal{R} \Phi_1^{1q's't'} \rangle_0 \\ &= n \langle v \rangle_0 \left[\bar{\sigma}' \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)} + \bar{\sigma}'' \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)} \right] \Delta^{(1)} \\ &= n \langle v \rangle_0 \tilde{\Theta} \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)} \Delta^{(1)}. \end{aligned} \quad (14)$$

Here, $\langle v \rangle_0 = 4(k_B T/\pi m)^{1/2}$ is the average relative thermal speed and $\bar{\sigma}' \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)}$, $\bar{\sigma}'' \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)}$ and $\tilde{\Theta} \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)}$ are temperature-dependent generalised cross sections. In this work, we use only barred cross sections [25,29], and the overbar will be omitted when the barred and unbarred cross sections are identical. Using Equations (12), (13) and (14), the system of linear equations (10) can now be written as

$$\begin{aligned} & \sum_{q's't'} \tilde{\Theta} \begin{pmatrix} 1q & s & t \\ 1q's't' \end{pmatrix}^{(1)} X^{1q's't'} \\ &= \frac{\delta_{q0}}{\langle v \rangle_0} (\delta_{s1} \delta_{t0} C^{1010} + \delta_{s0} \delta_{t1} C^{1001}). \end{aligned} \quad (15)$$

The thermal conductivity is obtained from the non-equilibrium average of the microscopic energy flux [25],

$$\begin{aligned} \mathbf{q} &= nk_B T \langle \Psi^E \rangle_{\text{ne}} = nk_B T \langle \Psi^E | \phi \rangle_0 \\ &= -k_B T \sum_{qst} \langle \Psi^E | \Phi_1^{1qst} \rangle_0 X^{1qst} \cdot \mathbf{X}^E = -\lambda \nabla T. \end{aligned} \quad (16)$$

It follows that

$$\lambda = \lambda_{\text{tr}} + \lambda_{\text{int}} = k_B C^{1010} X^{1010} + k_B C^{1001} X^{1001}. \quad (17)$$

To obtain the first-order approximation for the thermal conductivity, we need to consider only the basis vectors Φ^{1010} and Φ^{1001} in the expansion of the perturbation function ϕ . The system of linear equation (15) then becomes

$$\begin{aligned} \Theta(1010) X^{1010} + \Theta \begin{pmatrix} 1010 \\ 1001 \end{pmatrix} X^{1001} &= \frac{C^{1010}}{\langle v \rangle_0}, \\ \Theta \begin{pmatrix} 1001 \\ 1010 \end{pmatrix} X^{1010} + \Theta(1001) X^{1001} &= \frac{C^{1001}}{\langle v \rangle_0}, \end{aligned} \quad (18)$$

where $\Theta(10st) \equiv \Theta \begin{pmatrix} 10st \\ 10st \end{pmatrix}$. The result for the first-order approximation is

$$\begin{aligned} [\lambda]_1 &= [\lambda_{\text{tr}}]_1 + [\lambda_{\text{int}}]_1 \\ &= \frac{5k_B^2 T}{2m \langle v \rangle_0} \left(\frac{S_{11}^{(1)} - r S_{21}^{(1)}}{S^{(1)}} + \frac{r^2 S_{22}^{(1)} - r S_{12}^{(1)}}{S^{(1)}} \right), \end{aligned} \quad (19)$$

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

$$S^{(1)} = \begin{vmatrix} \Theta(1010) & \Theta \begin{pmatrix} 1010 \\ 1001 \end{pmatrix} \\ \Theta \begin{pmatrix} 1001 \\ 1010 \end{pmatrix} & \Theta(1001) \end{vmatrix}, \quad (20)$$

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

$$r = \frac{C^{1001}}{C^{1010}} = \left(\frac{2C_{\text{int}}}{5k_B} \right)^{1/2}. \quad (21)$$

Second-order approximations were derived by Kagan and Afanas'ev [30] and by Maitland *et al.* [31].

3. Obtaining thermal conductivity values for vibrationally excited molecules from rigid-rotor cross sections

Today the CT approach is the method of choice for computing generalised cross sections [32]. The colliding molecules are approximated as rigid rotors ($C_{\text{int,rr}} = C_{\text{rot}}$) in the CT calculations. General expressions for the rigid-rotor cross sections $\tilde{\Theta} \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}_{\text{rr}}^{(k)} = \bar{\sigma}' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}_{\text{rr}}^{(k)} + \bar{\sigma}'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}_{\text{rr}}^{(k)}$, suitable for numerical evaluation, have been provided by Curtiss [28] and Dickinson *et al.* [17] for linear and non-linear rigid rotors, respectively. However, the resulting thermal conductivity values λ_{rr} only account for translational and rotational energy transport. Using $C_{\text{int}} = C_{\text{rot}} + C_{\text{vib}}$ instead of $C_{\text{int,rr}} = C_{\text{rot}}$ in Equation (21) is not sufficient to fully account for vibrational effects.

Bich *et al.* [18] investigated the influence of vibrational excitation on the individual cross sections that enter the

first-order approximation of the thermal conductivity. Assuming that the vibrational states of the molecules do not change during a collision, and that the influence of the vibrational motion on the trajectories is negligible, they obtained

$$\mathfrak{S}(1010) = \mathfrak{S}(1010)_{\text{rr}}, \quad (22)$$

$$\mathfrak{S}\begin{pmatrix} 1010 \\ 1001 \end{pmatrix} = \left(\frac{C_{\text{rot}}}{C_{\text{int}}}\right)^{1/2} \mathfrak{S}\begin{pmatrix} 1010 \\ 1001 \end{pmatrix}_{\text{rr}}, \quad (23)$$

$$\mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix} = \left(\frac{C_{\text{rot}}}{C_{\text{int}}}\right)^{1/2} \mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix}_{\text{rr}}, \quad (24)$$

$$\mathfrak{S}(1001) = \frac{C_{\text{rot}}}{C_{\text{int}}} \mathfrak{S}(1001)_{\text{rr}} + \frac{C_{\text{vib}}}{C_{\text{int}}} \sigma'(1000)_{\text{rr}}. \quad (25)$$

The cross section $\sigma'(1000)_{\text{rr}}$ is related to the first-order approximation of the self-diffusion coefficient,

$$[\mathcal{D}_{\text{self,rr}}]_1 = \frac{k_{\text{B}}T}{\langle v \rangle_0 \sigma'(1000)_{\text{rr}}}. \quad (26)$$

This means that the vibrational energy is transported only by the movement of the molecules. Bock *et al.* [19] suggested to correct the additional cross sections needed to calculate higher order approximations using the approximate relationship

$$\tilde{\mathfrak{S}}\begin{pmatrix} 1qst \\ 1q's't' \end{pmatrix}^{(1)} \approx \left(\frac{C_{\text{rot}}}{C_{\text{int}}}\right)^{(t+t')/2} \tilde{\mathfrak{S}}\begin{pmatrix} 1qst \\ 1q's't' \end{pmatrix}_{\text{rr}}^{(1)}. \quad (27)$$

Relations (22)–(25) and (27) were utilised in Refs [19–24] to calculate the thermal conductivities of CO₂, CH₄, H₂O, H₂S and N₂ in the dilute-gas limit. The agreement with the best experimental data is satisfactory in most cases. A striking exception are the strong systematic deviations found for H₂O at high temperatures [24], indicating that there might be deficiencies in the kinetic theory approach used so far.

One of the shortcomings is the use of a single Wang Chang–Uhlenbeck polynomial for the total reduced internal energy \mathcal{E}_{int} in the basis functions Φ_k^{pqst} . In order to increase the flexibility of the basis functions, it has been suggested [13,33–35] to use a product of Wang Chang–Uhlenbeck polynomials for the different internal degrees of freedom. First-order expressions for the thermal conductivity have been derived using such an approach for both pure gases [13,33] and gas mixtures [35].

We follow this approach and define basis functions Φ_k^{pqstu} as products of rigid-rotor basis functions $\Phi_{k,\text{rr}}^{pqst}$ and normalised Wang Chang–Uhlenbeck polynomials of order

u in the total reduced vibrational energy \mathcal{E}_{vib} ,

$$\Phi_k^{pqstu} = \Phi_{k,\text{rr}}^{pqst} R_u(\mathcal{E}_{\text{vib}}). \quad (28)$$

The normalised Wang Chang–Uhlenbeck polynomials satisfy the orthogonality condition

$$\langle R_u(\mathcal{E}_{\text{vib}}) | R_{u'}(\mathcal{E}_{\text{vib}}) \rangle_0 = \delta_{uu'}. \quad (29)$$

The first two polynomials are

$$R_0(\mathcal{E}_{\text{vib}}) = 1, \quad (30)$$

$$R_1(\mathcal{E}_{\text{vib}}) = \left(\frac{k_{\text{B}}}{C_{\text{vib}}}\right)^{1/2} (\mathcal{E}_{\text{vib}} - \langle \mathcal{E}_{\text{vib}} \rangle_0). \quad (31)$$

Using the basis functions Φ_k^{pqstu} , the heat flux Ψ^E is given as a sum of three contributions,

$$\begin{aligned} \Psi^E &= \Psi_{\text{tr}}^E + \Psi_{\text{rot}}^E + \Psi_{\text{vib}}^E \\ &= C^{10100} \Phi^{10100} + C^{10010} \Phi^{10010} + C^{10001} \Phi^{10001}, \end{aligned} \quad (32)$$

where $C^{10100} = (5k_{\text{B}}T/2m)^{1/2}$, $C^{10010} = (C_{\text{rot}}T/m)^{1/2}$ and $C^{10001} = (C_{\text{vib}}T/m)^{1/2}$. The generalisation of the system of linear equation (15) is given by

$$\begin{aligned} \sum_{q's't'u'} \tilde{\mathfrak{S}}\begin{pmatrix} 1qst \\ 1q's't'u' \end{pmatrix}^{(1)} X^{1q's't'u'} \\ = \frac{\delta_{q0}}{\langle v \rangle_0} (\delta_{s1} \delta_{t0} \delta_{u0} C^{10100} + \delta_{s0} \delta_{t1} \delta_{u0} C^{10010} \\ + \delta_{s0} \delta_{t0} \delta_{u1} C^{10001}). \end{aligned} \quad (33)$$

The thermal conductivity is then obtained as

$$\begin{aligned} \lambda &= \lambda_{\text{tr}} + \lambda_{\text{rot}} + \lambda_{\text{vib}} \\ &= k_{\text{B}} C^{10100} X^{10100} + k_{\text{B}} C^{10010} X^{10010} \\ &\quad + k_{\text{B}} C^{10001} X^{10001}. \end{aligned} \quad (34)$$

For the first-order approximation, we need to consider the basis vectors Φ^{10100} , Φ^{10010} and Φ^{10001} , and obtain

$$\begin{aligned} \mathfrak{S}(10100) X^{10100} + \mathfrak{S}\begin{pmatrix} 10100 \\ 10010 \end{pmatrix} X^{10010} \\ + \mathfrak{S}\begin{pmatrix} 10100 \\ 10001 \end{pmatrix} X^{10001} = \frac{C^{10100}}{\langle v \rangle_0}, \\ \mathfrak{S}\begin{pmatrix} 10010 \\ 10100 \end{pmatrix} X^{10100} + \mathfrak{S}(10010) X^{10010} \end{aligned}$$

$$\begin{aligned}
& + \mathfrak{S} \begin{pmatrix} 10010 \\ 10001 \end{pmatrix} X^{10001} = \frac{C^{10010}}{\langle v \rangle_0}, \\
& \mathfrak{S} \begin{pmatrix} 10001 \\ 10100 \end{pmatrix} X^{10100} + \mathfrak{S} \begin{pmatrix} 10001 \\ 10010 \end{pmatrix} X^{10010} \\
& + \mathfrak{S}(10001) X^{10001} = \frac{C^{10001}}{\langle v \rangle_0}. \quad (35)
\end{aligned}$$

If the vibrational states of the molecules do not change during collisions, and if the influence of the vibrational motion on the trajectories is negligible (the same assumptions as in the approach of Bich and co-workers [18,19]), it can be shown that

$$\begin{aligned}
\bar{\sigma}' \begin{pmatrix} p q s t u \\ p' q' s' t' u' \end{pmatrix}^{(k)} &= \bar{\sigma}' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)} \langle R_u(\mathcal{E}_{\text{vib}}) | R_{u'}(\mathcal{E}_{\text{vib}}) \rangle_0 \\
&= \bar{\sigma}' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)} \delta_{uu'}, \quad (36)
\end{aligned}$$

$$\begin{aligned}
\bar{\sigma}'' \begin{pmatrix} p q s t u \\ p' q' s' t' u' \end{pmatrix}^{(k)} &= \bar{\sigma}'' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)} \\
&\times \langle R_u(\mathcal{E}_{\text{vib}}) \rangle_0 \langle R_{u'}(\mathcal{E}_{\text{vib}}) \rangle_0 \\
&= \bar{\sigma}'' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)} \delta_{u0} \delta_{u'0}. \quad (37)
\end{aligned}$$

Thus, the cross sections $\tilde{\mathfrak{S}} \begin{pmatrix} p q s t u \\ p' q' s' t' u' \end{pmatrix}^{(k)}$ can be expressed in terms of the rigid-rotor cross sections $\tilde{\mathfrak{S}} \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)}$ and $\bar{\sigma}' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)}$,

$$\tilde{\mathfrak{S}} \begin{pmatrix} p q s t 0 \\ p' q' s' t' 0 \end{pmatrix}^{(k)} = \tilde{\mathfrak{S}} \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)}, \quad (38)$$

$$\begin{aligned}
\tilde{\mathfrak{S}} \begin{pmatrix} p q s t u \\ p' q' s' t' u' \end{pmatrix}^{(k)} &= \bar{\sigma}' \begin{pmatrix} p q s t \\ p' q' s' t' \end{pmatrix}_{\text{rr}}^{(k)} \delta_{uu'}, \\
&u + u' \geq 1. \quad (39)
\end{aligned}$$

The system of linear equation (35) then becomes

$$\begin{aligned}
\mathfrak{S}(1010)_{\text{rr}} X^{10100} + \mathfrak{S} \begin{pmatrix} 1010 \\ 1001 \end{pmatrix}_{\text{rr}} X^{10010} &= \frac{C^{10100}}{\langle v \rangle_0}, \\
\mathfrak{S} \begin{pmatrix} 1001 \\ 1010 \end{pmatrix}_{\text{rr}} X^{10100} + \mathfrak{S}(1001)_{\text{rr}} X^{10010} &= \frac{C^{10010}}{\langle v \rangle_0}, \\
\sigma'(1000)_{\text{rr}} X^{10001} &= \frac{C^{10001}}{\langle v \rangle_0}. \quad (40)
\end{aligned}$$

Solving the first two equations for X^{10100} and X^{10010} , and substituting into Equation (34) yields the rigid-rotor thermal conductivity $[\lambda_{\text{rr}}]_1$. From the third equation, we obtain the vibrational contribution,

$$\begin{aligned}
[\lambda_{\text{vib}}]_1 &= k_{\text{B}} C^{10001} X^{10001} = \frac{C_{\text{vib}} k_{\text{B}} T}{m \langle v \rangle_0 \sigma'(1000)_{\text{rr}}} \\
&= [\mathcal{D}_{\text{self,rr}}]_1 c_{\text{vib}}. \quad (41)
\end{aligned}$$

Thus, the total thermal conductivity is now given as

$$[\lambda]_1 = [\lambda_{\text{rr}}]_1 + [\mathcal{D}_{\text{self,rr}}]_1 c_{\text{vib}}. \quad (42)$$

To obtain a second-order approximation, $[\lambda]_2$, we consider the basis vectors Φ^{10100} , Φ^{10010} , Φ^{10001} , Φ^{10200} , Φ^{10020} , Φ^{10110} , Φ^{10101} , Φ^{10011} , Φ_1^{12000} and Φ_1^{11000} . Using Equations (38) and (39), we obtain two independent systems of linear equations, one for the rigid-rotor contribution, $[\lambda_{\text{rr}}]_2$, and one for the vibrational contribution, $[\lambda_{\text{vib}}]_2$. The rigid-rotor part is given by

$$[\lambda_{\text{rr}}]_2 = \frac{5k_{\text{B}}^2 T}{2m \langle v \rangle_0} \left(\frac{S_{11}^{(2)} - r S_{21}^{(2)}}{S^{(2)}} + \frac{r^2 S_{22}^{(2)} - r S_{12}^{(2)}}{S^{(2)}} \right), \quad (43)$$

with $r = (2C_{\text{rot}}/5k_{\text{B}})^{1/2}$ and

$$S^{(2)} = \begin{vmatrix} \mathfrak{S}(1010)_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1010 \\ 1001 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1010 \\ 1020 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1010 \\ 1011 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1010 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1010 \\ 1200 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1010 \\ 1100 \end{pmatrix}_{\text{rr}} \\ \mathfrak{S} \begin{pmatrix} 1001 \\ 1010 \end{pmatrix}_{\text{rr}} & \mathfrak{S}(1001)_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1001 \\ 1020 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1001 \\ 1011 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1001 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1001 \\ 1200 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1001 \\ 1100 \end{pmatrix}_{\text{rr}} \\ \mathfrak{S} \begin{pmatrix} 1020 \\ 1010 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1020 \\ 1001 \end{pmatrix}_{\text{rr}} & \mathfrak{S}(1020)_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1020 \\ 1011 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1020 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1020 \\ 1200 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1020 \\ 1100 \end{pmatrix}_{\text{rr}} \\ \mathfrak{S} \begin{pmatrix} 1011 \\ 1010 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1011 \\ 1001 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1011 \\ 1020 \end{pmatrix}_{\text{rr}} & \mathfrak{S}(1011)_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1011 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1011 \\ 1200 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1011 \\ 1100 \end{pmatrix}_{\text{rr}} \\ \mathfrak{S} \begin{pmatrix} 1002 \\ 1010 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1002 \\ 1001 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1002 \\ 1020 \end{pmatrix}_{\text{rr}} & \mathfrak{S} \begin{pmatrix} 1002 \\ 1011 \end{pmatrix}_{\text{rr}} & \mathfrak{S}(1002)_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1002 \\ 1200 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1002 \\ 1100 \end{pmatrix}_{\text{rr}} \\ \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1010 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1001 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1020 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1011 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}}(1200)_{\text{rr}}^{(1)} & \tilde{\mathfrak{S}} \begin{pmatrix} 1200 \\ 1100 \end{pmatrix}_{\text{rr}}^{(1)} \\ \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1010 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1001 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1020 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1011 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1002 \end{pmatrix}_{\text{rr}} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1200 \end{pmatrix}_{\text{rr}}^{(1)} & \tilde{\mathfrak{S}} \begin{pmatrix} 1100 \\ 1100 \end{pmatrix}_{\text{rr}}^{(1)} \end{vmatrix}. \quad (44)$$

For the vibrational part, we have

$$[\lambda_{\text{vib}}]_2 = \frac{C_{\text{vib}} k_B T}{m \langle v \rangle_0} \frac{S'_{11}{}^{(2)}}{S'^{(2)}} = [D_{\text{self,rr}}]_2 c_{\text{vib}}, \quad (45)$$

where

$$S'^{(2)} = \begin{vmatrix} \sigma'(1000)_{\text{rr}} & \sigma'(1000)_{1010\text{rr}} & \sigma'(1000)_{1001\text{rr}} & \bar{\sigma}'(1000)_{1200\text{rr}} & \bar{\sigma}'(1000)_{1100\text{rr}} \\ \sigma'(1010)_{1000\text{rr}} & \sigma'(1010)_{\text{rr}} & \sigma'(1010)_{1001\text{rr}} & \bar{\sigma}'(1010)_{1200\text{rr}} & \bar{\sigma}'(1010)_{1100\text{rr}} \\ \sigma'(1001)_{1000\text{rr}} & \sigma'(1001)_{1010\text{rr}} & \sigma'(1001)_{\text{rr}} & \bar{\sigma}'(1001)_{1200\text{rr}} & \bar{\sigma}'(1001)_{1100\text{rr}} \\ \bar{\sigma}'(1200)_{1000\text{rr}} & \bar{\sigma}'(1200)_{1010\text{rr}} & \bar{\sigma}'(1200)_{1001\text{rr}} & \bar{\sigma}'(1200)_{\text{rr}}^{(1)} & \bar{\sigma}'(1200)_{1100\text{rr}}^{(1)} \\ \bar{\sigma}'(1100)_{1000\text{rr}} & \bar{\sigma}'(1100)_{1010\text{rr}} & \bar{\sigma}'(1100)_{1001\text{rr}} & \bar{\sigma}'(1100)_{1200\text{rr}}^{(1)} & \bar{\sigma}'(1100)_{1100\text{rr}}^{(1)} \end{vmatrix}. \quad (46)$$

The total thermal conductivity is again the sum of both contributions,

$$[\lambda]_2 = [\lambda_{\text{rr}}]_2 + [D_{\text{self,rr}}]_2 c_{\text{vib}}. \quad (47)$$

To the best of our knowledge, only the first-order approximation (26) was previously known for the self-diffusion coefficient of a molecular gas. Note the similarity of Equations (42) and (47) with the modified Eucken formula (2).

4. Results and discussion

We have re-evaluated the thermal conductivities of carbon dioxide [19], methane [20], water vapour [24], hydrogen sulphide [21,22] and nitrogen [23] in the dilute-gas limit using the new approach. For hydrogen sulphide and water vapour, we have also improved the precision of the generalised cross sections by increasing the number of classical trajectories by about a factor of 4 for H₂S, and about a factor of 5 for H₂O. The trajectories and the generalised cross sections have been computed using an extended version of the TRAJECT software code [16,17]. In the present CT calculations for H₂O, we have used the CC-pol *ab initio* pair potential of Bukowski and co-workers [36,37]. Of the four pair potentials tested in Ref. [24], it gave the best agreement with accurate experimental data for the shear viscosity of dilute water vapour.

For CH₄, N₂ and CO₂, the new thermal conductivity values agree to better than $\pm 0.15\%$ with the values resulting from the procedure of Bich and co-workers [18,19]. However, for H₂S and H₂O, the new values differ by up to +1.0% and +5.6%, respectively. The values resulting from the different approaches are given for H₂S in Table 1, and for H₂O in Table 2. The C_V values listed in the tables have been calculated using the recommended equations of state [38,39].

There are only very few experimental data-sets for the thermal conductivity of H₂S vapour. The data of Correia *et al.* [40] for temperatures between 277 K and 594 K were found to be of high quality [21], with deviations of +1.2%

to +1.8% from the theoretically calculated values of Ref. [21]. Using the more precise values of the generalised cross sections from the present CT calculations, we obtain deviations of +1.0% to +1.6% for the procedure of Bich and co-workers. If we apply the new approach, the deviations are reduced to only +0.3% to +0.8%.

The thermal conductivity of water vapour has been extensively studied experimentally. In Figure 1, calculated values are compared with selected experimental data [41–49] as well as with the two most recent correlations of the International Association for the Properties of Water and Steam (IAPWS) [50,51]. The values obtained with the procedure of Bich and co-workers progressively underestimate the experimental data with increasing temperature, whereas the values resulting from the approach of this paper show excellent agreement with the experimental data for all temperatures. Note that the thermal conductivity values of Ref.

Table 1. Thermal conductivity (in mW m⁻¹ K⁻¹) of dilute hydrogen sulphide gas calculated using the rigid-rotor approach ($[\lambda_{\text{rr}}]_1$, $[\lambda_{\text{rr}}]_2$), the approach of Bich and co-workers [18,19] ($[\lambda_{\text{B}}]_1$, $[\lambda_{\text{B}}]_2$) and the approach of this paper ($[\lambda]_1$, $[\lambda]_2$).

T/K	C_V/R	$[\lambda_{\text{rr}}]_1$	$[\lambda_{\text{B}}]_1$	$[\lambda]_1$	$[\lambda_{\text{rr}}]_2$	$[\lambda_{\text{B}}]_2$	$[\lambda]_2$
180	3.01	8.05	8.07	8.07	8.07	8.09	8.09
200	3.01	8.97	9.00	9.00	8.99	9.03	9.03
225	3.03	10.14	10.21	10.22	10.17	10.24	10.25
250	3.05	11.34	11.48	11.50	11.37	11.51	11.53
275	3.07	12.56	12.80	12.83	12.60	12.84	12.87
300	3.10	13.79	14.18	14.22	13.84	14.22	14.27
325	3.14	15.03	15.60	15.67	15.09	15.66	15.72
350	3.18	16.28	17.07	17.16	16.35	17.14	17.22
375	3.23	17.53	18.59	18.70	17.60	18.67	18.78
400	3.27	18.78	20.14	20.29	18.86	20.23	20.37
450	3.37	21.26	23.36	23.56	21.36	23.48	23.67
500	3.48	23.70	26.70	26.96	23.83	26.84	27.09
550	3.58	26.10	30.14	30.46	26.25	30.32	30.61
600	3.69	28.46	33.69	34.05	28.63	33.90	34.23
650	3.80	30.77	37.31	37.72	30.97	37.56	37.92
700	3.91	33.03	41.02	41.45	33.26	41.29	41.69
750	4.02	35.24	44.77	45.23	35.50	45.09	45.50
800	4.13	37.41	48.58	49.05	37.69	48.92	49.35
900	4.33	41.61	56.26	56.75	41.95	56.67	57.11
1000	4.52	45.66	63.97	64.45	46.05	64.43	64.87
1100	4.70	49.56	71.62	72.08	50.00	72.12	72.56
1200	4.85	53.33	79.16	79.59	53.81	79.71	80.14
1400	5.12	60.53	93.77	94.15	61.09	94.40	94.81
1600	5.32	67.29	107.7	108.0	67.93	108.4	108.8
1800	5.49	73.64	120.8	121.1	74.36	121.6	122.0
2000	5.62	79.60	133.3	133.6	80.41	134.1	134.6

Table 2. Thermal conductivity (in $\text{mW m}^{-1} \text{K}^{-1}$) of dilute water vapour calculated using the rigid-rotor approach ($[\lambda_{rr}]_1$, $[\lambda_{rr}]_2$), the approach of Bich and co-workers [18,19] ($[\lambda_B]_1$, $[\lambda_B]_2$) and the approach of this paper ($[\lambda]_1$, $[\lambda]_2$).

T/K	C_V/R	$[\lambda_{rr}]_1$	$[\lambda_B]_1$	$[\lambda]_1$	$[\lambda_{rr}]_2$	$[\lambda_B]_2$	$[\lambda]_2$
250	3.02	14.89	14.96	14.98	15.03	15.10	15.12
275	3.03	16.53	16.64	16.67	16.68	16.79	16.83
300	3.04	18.20	18.38	18.43	18.36	18.54	18.59
325	3.06	19.91	20.17	20.25	20.07	20.34	20.42
350	3.07	21.65	22.03	22.15	21.82	22.21	22.33
375	3.10	23.43	23.97	24.13	23.61	24.16	24.32
400	3.12	25.25	25.98	26.21	25.44	26.18	26.40
450	3.18	28.99	30.22	30.62	29.20	30.45	30.83
500	3.24	32.87	34.75	35.36	33.09	35.01	35.60
550	3.30	36.85	39.54	40.44	37.09	39.83	40.69
600	3.37	40.90	44.57	45.80	41.17	44.91	46.09
650	3.44	45.01	49.82	51.44	45.31	50.21	51.75
700	3.51	49.15	55.28	57.33	49.47	55.71	57.67
750	3.58	53.30	60.92	63.44	53.65	61.42	63.81
800	3.66	57.44	66.74	69.75	57.83	67.30	70.17
900	3.81	65.65	78.85	82.92	66.12	79.58	83.43
1000	3.96	73.71	91.53	96.67	74.29	92.45	97.29
1100	4.12	81.60	104.7	110.8	82.30	105.8	111.6
1200	4.26	89.30	118.1	125.3	90.13	119.5	126.2
1300	4.41	96.81	131.9	139.9	97.79	133.5	140.9
1400	4.54	104.1	145.7	154.5	105.3	147.6	155.7
1600	4.78	118.3	173.7	183.5	119.8	176.0	185.1
1800	4.98	132.0	201.4	211.9	133.7	204.2	213.9
2000	5.16	145.2	228.7	239.6	147.2	231.9	241.9
2250	5.33	161.2	262.0	273.0	163.5	265.7	275.8
2500	5.48	176.7	294.4	305.2	179.3	298.4	308.3

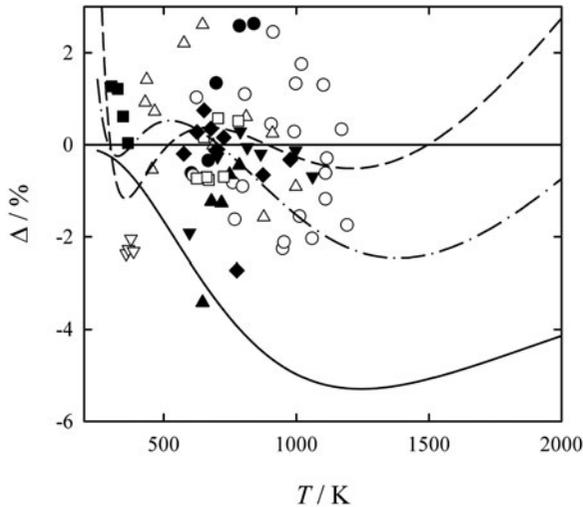


Figure 1. Deviations, $\Delta = (\lambda - [\lambda]_2)/[\lambda]_2$, of experimental data, of experimentally based correlations and of values calculated using the procedure of Bich and co-workers [18,19] from values calculated using the approach of this paper for the thermal conductivity of dilute water vapour as a function of temperature: \bullet , Vargaftik and Tarzimanov [41]; \circ , Vargaftik and Zimina [42]; \blacktriangle , Le Neindre *et al.* [43]; \triangle , Vargaftik *et al.* [44]; \blacktriangledown , Popov and Dulnev [45]; ∇ , Curtiss *et al.* [46]; \blacksquare , Miroshnichenko and Makhrov [47]; \square , Tufeu and Le Neindre [48]; \blacklozenge , Tarzimanov and Gabitov [49]; ---, IAPWS 2008 [50]; - · -, IAPWS 2011 [51]; —, $[\lambda]_2$ values from the procedure of Bich and co-workers [18,19].

[24] (obtained with the approach of Bich and co-workers) were used in the development of the IAPWS 2011 [51] correlation to supplement the experimental data-sets at very low and very high temperatures [52].

Apparently, the approach of Bich and co-workers works well only for non-polar gases. In such gases, mostly translational energy is exchanged during collisions. By contrast, in polar gases significant exchange of rotational energy occurs due to the long-range electrostatic interactions, whereas changes in the vibrational energy levels are still rare (and neglected in the approaches of Bich and co-workers and of this paper). It is therefore reasonable to assume that the non-equilibrium distribution function behaves differently with respect to the rotational and vibrational energies. If we use the basis functions Φ_k^{pqst} , the non-equilibrium distribution function depends only on the total internal energies of the molecules. On the other hand, the basis functions of this paper, Φ_k^{pqstu} , allow to distinguish between rotational and vibrational degrees of freedom, so that the non-equilibrium distribution function can be approximated more accurately.

One weakness of our new approach is that it does not account for vibrationally inelastic and vibrationally resonant collisions. In fact, for water vapour vibrationally inelastic collisions occur more often than for most other gases [53,54]. However, since the agreement of the calculated thermal conductivity values for water vapour with the experimental data is already excellent, we expect that the effect on the thermal conductivity is rather small.

We estimate the uncertainty of the $[\lambda]_2$ values for dilute water vapour (last column of Table 2) to be of the order of $\pm 2\%$ for temperatures between 500 and 1000 K, increasing to $\pm 4\%$ at 250 K and 2500 K. For dilute hydrogen sulphide, we estimate the uncertainties to be of the order of $\pm 1\%$ between 300 and 500 K, increasing to $\pm 2\%$ at 180 K and 2000 K. Note that these uncertainty estimates do not take into account an increase of the thermal conductivity due to partial dissociation [55] at high temperatures.

5. Conclusions

We have presented a new kinetic theory approach for calculating the thermal conductivity of a dilute polyatomic gas. In contrast to the previously used approach of Bich and co-workers [18,19], the new method utilises more flexible basis functions that contain separate polynomials for the rotational and vibrational energies instead of a single polynomial for the total internal energy of a molecule. The resulting first- and second-order expressions for the thermal conductivity involve only the vibrational heat capacity, as well as generalised cross sections that can be computed using the CT method for rigid rotors. We have also obtained a second-order expression for the self-diffusion coefficient.

The new approach has been tested by calculating the thermal conductivity of methane, nitrogen, carbon dioxide, hydrogen sulphide and water vapour in the dilute-gas limit. While for methane, nitrogen and carbon dioxide, the

resulting values agree within $\pm 0.15\%$ with those obtained using the method of Bich and co-workers, the values for hydrogen sulphide and water vapour differ by up to $+1.0\%$ and $+5.6\%$, respectively. For both gases, the agreement with experimental data is substantially improved.

Although we have only considered pure gases in this work, the extension of the new approach to gas mixtures is straightforward and will be published separately.

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