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Theoretical evaluation of diffusion coefficients of $(Al_2O_3)_n$ clusters in different bath gases

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Abstract. The binary diffusion coefficients of two low lying isomers of $(Al_2O_3)_n$, $n = 1 \ldots 4$, clusters in different bath gases, that most frequently met in the nature and in the technical applications: H_2, N_2, O_2, CO, H_2O as well as their self-diffusion coefficients have been calculated on the basis of kinetic theory and dipole reduced formalism. The parameters of interaction potential have been determined taking into account the contributions of a dispersion, dipole-dipole and dipole-induced dipole interactions between alumina clusters and bath molecules. The dipole moments, polarizabilities and collision diameters of clusters have been obtained by using quantum chemical calculations of cluster structure. The approximations for temperature dependencies of diffusion coefficients for two low-lying isomers of each considered alumina clusters are reported. It is demonstrated that an account for the contributions of the second for each type of clusters does not affect substantially the value of net diffusion coefficient. The diffusion coefficients of the isomers of small $(Al_2O_3)_n$ clusters can differ notably in the case when their dipole moments are distinct and they interact with strongly dipole molecules.

1 Introduction

For past decade an explosion of interest in the investigation of structure and physical properties of nanoclusters has been driven by the fact that clusters form in various nature phenomena and that they have wide-range applications for the fabrication of novel nanomaterials for electronics, catalysis, medicine, aerospace vehicles, energy conversion, etc. So, nanoclusters are observed in the upper atmosphere of different planets [1], they participate in the astrophysical dust formation processes [1,2] and form during the combustion of hydrocarbon and metallized fuels [3–6] and energetic materials [7,8]. As well, nanoclusters play an important role in plasma etching [9], plasma-based technologies [10,11] and chemical vapor deposition upon laser ablation [10,12,13]. Simulations of these processes require the data on thermodynamic and transport properties of such clusters.

Today, there are no appropriate experimental approaches and diagnostic systems allowing one to measure directly the thermodynamic and transport properties of nanoclusters. At the same time, the modern theoretical approaches make it possible to estimate the needed parameters on the basis of quantum chemical calculations. Such calculations allow one to build the potential energy surfaces (PESs) for atomic system relevant to clusters and to find the minima on the PESs corresponding to possible isomers of clusters. Therefore, one can determine their electronic energy, frequencies of normal vibrations, rotational constants, electronic degeneracy, geometric structure and collision diameter. This information enables to estimate thermodynamic properties such as temperature-dependent enthalpy, entropy, specific heat capacity and Gibbs energy.

In order to estimate the transport properties, such as diffusion, thermal conductivity and viscosity coefficients, it is necessary to find the potential energy of the interaction of clusters with bath gases or other clusters. In common case, the special efforts are needed to determine the interaction potential for a given type of cluster. However, frequently, it is supposed that nanoclusters interact as ordinary molecules via the Stockmayer (SM) 12-6-3 potential for the case of polar clusters and well-known Lennard-Jones (LJ) 12-6 potential for the interaction of nonpolar ones [14,15]. Usually, the parameters of these types of potential are obtained via fitting the predictions and experimental data on such macroscopic parameters as second virial coefficient, coefficients of viscosity and thermal conductivity [14].

On the other hand, the parameters of intermolecular potential can be derived from the extensive ab initio calculations of the potential energy surface on a large grid of

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molecular geometries [16,17]. However, the adequate ab initio description of long-range intermolecular forces requires the use of rather expensive post-Hartree-Fock methods for solving the Schrödinger equation with large and flexible basis sets, that makes the whole procedure computationally expensive, especially, for large molecules and molecular clusters [18]. That is why, the usage of analytic and empiric approaches for finding the PES to estimate interaction potential is desirable even for small clusters.

The present paper addresses the evaluation of diffusion coefficients of $(\mathrm{Al_2O_3})_n$, $n = 1\ldots4$, clusters with different bath gases most frequently occurring in the applications, such as $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, CO and $\mathrm{H_2O}$, on the basis of quantum-chemical calculations of cluster physical properties. It is worth noting that aluminum oxide is one of the most important and widespread oxygen-bearing compounds. Alumina is a constituent in a number of ceramic materials. Alumina clusters and particles are formed during the combustion of Al powder in various environments: air [4], steam [19], carbon dioxide [19,20] as well as during the combustion of different energetic materials [21]. In addition, $(\mathrm{Al_2O_3})_n$ clusters were observed in astrophysical dust [22]. In order to model these processes and phenomena the diffusion coefficients for $(\mathrm{Al_2O_3})_n$ clusters are strongly needed. However, until now there is no information about transport properties of small alumina clusters.

2 Methodology

2.1 Binary diffusion coefficient and collision integrals

In principle, the traditional kinetic theory allows one to estimate the transport properties of individual species, if the potential energy of particle interaction is known. The binary diffusion coefficients D_{ij} can be calculated with the use of known equation obtained on the basis of Chapman-Enskog theory [14,23] and applicable at low and moderate pressures

$$D_{ij} = \frac{3}{8}\frac{\sqrt{2\pi M_{ij}kT/N_\mathrm{A}}}{\pi\sigma_{ij}^2}\frac{1}{\Omega^{(1,1)^*}}\frac{RT}{P_0 2M_{ij}},$$
$$M_{ij} = \frac{M_i M_j}{M_i + M_j}. \tag{1}$$

Here $M_{i(j)}$ is the molar mass of particles of $i(j)$ sort, T is the temperature, k is the Boltzmann constant, N_A is the Avogadro number, σ_{ij} is the collision diameter of colliding particles, P_0 is the normal atmospheric pressure, $\Omega^{(1,1)^*}$ is the reduced collision integral normalized by the cross sections for rigid spheres of diameter σ_{ij}. In fact, the product $f = \sigma_{ij}^2\Omega^{(1,1)^*}(T)$ is the energy-averaged cross-section that depends on the temperature and interparticle potential $\varphi_{ij}(r)$. Therefore, in order to estimate the value of D_{ij} one needs to know the parameters of potential $\varphi_{ij}(r)$.

As is known, for non-polar molecules the intermolecular interaction can be described by the LJ (12-6) potential

$$\varphi_{ij}^{LJ}(r) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right), \tag{2}$$

where the potential well depth can be expressed as

$$\varepsilon_{ij} = \frac{C_6^{disp}}{4\sigma_{ij}^6}. \tag{3}$$

The dispersion part of potential φ_{disp} is governed by the Slater-Kirkwood equation [24] in the spherically symmetric form:

$$\varphi_{disp}(r) = -\frac{C_6^{disp}}{r^6}, \quad C_6^{disp} = \frac{3}{2}E_{at}a_0^{3/2}\frac{\alpha_\mathrm{A}\alpha_\mathrm{B}}{\sqrt{\frac{\alpha_\mathrm{A}}{N_\mathrm{A}}} + \sqrt{\frac{\alpha_\mathrm{B}}{N_\mathrm{B}}}}. \tag{4}$$

Here $E_{at} = 27.211$ eV, a_0 is the Bohr radius, α_A and α_B are the polarizabilities, N_A and N_B are the numbers of valence electrons (the number of electrons in the outer sub-shell of particle) of particles of A and B sorts, r is the distance between interacting particles.

The collision integrals for LJ potential depend on the reduced temperature $T_{ij}^* = kT/\varepsilon_{ij}$, and the values of $\Omega^{(1,1)^*}(T_{ij}^*)$ were calculated and tabulated elsewhere [14,25–28]. Note that earlier the phenomenological approach based on the usage of Pirani's potential [29] was extensively used for the estimation of collision integrals relevant to the transport properties of atmospheric gases for the extremely broad temperature range ($T = 10^2$–10^5 K) [30,31]. However, in the present work, we used the approximations of collision integrals reported in reference [25] for LJ potential and applicable at the reduced temperature range $0.3 \leqslant T^* \leqslant 100$ ($T \leqslant 10^4$ K).

Note, that the Slater-Kirkwood equation commonly overestimates slightly the value of the dispersion term C_6^{disp} with respect to well-known London one [15]. However, equations (2)–(4) give, strictly speaking, only the estimates for long-range attractive potential. The exchange effects also should be taken into account at interparticle distance smaller than $15a_0$ [15], and, therefore, the potential well depth ε_{ij} can be potentially larger in this case. One can suppose that slight overestimation of dispersion term by the Slater-Kirkwood equation can be effectively compensated by neglecting the exchange forces.

In the case when molecules or clusters are polar, the angle-dependent dipole-induced dipole and dipole-dipole interactions also must be taken into account [14]. When these contributions are averaged over possible orientations of dipole moments of particles, the attractive potential between neutral species can be expressed as [15,28]

$$\varphi(r) = -\frac{C_6^{summ}}{r^6}, \tag{5}$$

where C_6^{summ} coefficient is the sum of the terms:

$$C_6^{summ} = C_6^{el} + C_6^{ind} + C_6^{disp}. \tag{6}$$

Here C_6^{el} and C_6^{ind} specify the orientation-averaged potential of electrostatic interaction of dipoles and the potential of polarization interaction. They are governed by the relationships

$$C_6^{el} = \frac{2}{3kT}\mu_\mathrm{A}^2\mu_\mathrm{B}^2, \tag{7}$$
$$C_6^{ind} = \mu_\mathrm{A}^2\alpha_\mathrm{B} + \mu_\mathrm{B}^2\alpha_\mathrm{A}. \tag{8}$$

Thus, the contributions of orientation-dependent dipole-induced dipole and dipole-dipole interactions to the values of collision integrals can be approximately estimated if the effective potential well depth is taken in the form

$$\varepsilon_{ij} = \frac{C_6^{el} + C_6^{ind} + C_6^{disp}}{4\sigma_{ij}^6}. \tag{9}$$

It is worth noting, that the procedure of direct summation of orientation-averaged terms responsible for the dipole-induced dipole and dipole-dipole interactions in the manner of equation (6) seems to be somewhat questionable. In practice, SM (12-6-3) potential is frequently used for the approximation of real interaction between two polar molecules of i and j sorts

$$\varphi_{ij}^{SM}(r) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left[1 + \xi_{ij}^{*}\zeta_{d-id}(\omega_{ij})\right]\left(\frac{\sigma_{ij}}{r}\right)^{6} - \delta_{ij}^{*}\zeta_{d-d}(\omega_{ij})\left(\frac{\sigma_{ij}}{r}\right)^{3}\right). \tag{10}$$

Here ζ_{d-id} and ζ_{d-d} are the angle-dependent functions for dipole-induced dipole and dipole-dipole types of interaction, ξ_{ij}^{*} and $\delta_{ij}^{*} = \mu_i\mu_j/2\varepsilon_{ij}\sigma_{ij}^3$ are the mean reduced polarizability and mean reduced dipole moments of interacting particles. In terms of the method of dipole reduced formalism (DRFM) developed by Paul and Warnatz [32], the potential φ_{ij}^{SM} subjected to thermally orientation-averaged procedure can be reduced to the effective LJ potential. This allows one to incorporate the dipole-dipole and dipole-induced dipole interaction terms into the methodology of reduced collision integrals developed originally for van der Waals potential. In this case, for the determination of effective potential parameters C_6^{eff} and σ_{ij}^{eff} the following equations are valid:

$$C_6^{eff} = C_6^{disp}\left(1 + \frac{C_6^{ind}}{C_6^{disp}} + \frac{C_6^{el}}{4C_6^{disp}}\right)^2, \tag{11}$$

$$\sigma_{ij}^{eff} = \sigma_{ij}\left(1 + \frac{C_6^{ind}}{C_6^{disp}} + \frac{C_6^{el}}{4C_6^{disp}}\right)^{-\frac{1}{6}}. \tag{12}$$

Note that for the realistic values of C_6^{el} and C_6^{ind} coefficients, the effective C_6^{eff} coefficient is smaller than the C_6^{summ} one, whereas the relation $\sigma_{ij}^{eff} \leqslant \sigma_{ij}$ is valid in any case.

2.2 Collision diameter of clusters

The collision diameter σ_{ij}, that specifies the range of repulsive valence forces for the LJ potential, is an important parameter which used for estimating the collision frequency, characteristic time of rotational relaxation, diffusion and viscosity coefficients, etc. In view of the absence of data on σ_{ij} for $(Al_2O_3)_n$ clusters in various bath gases, it is necessary to estimate the values of σ_{ij} theoretically.

Table 1. The values of static polarizability of atoms reported in reference [39] and used for estimating the LJ potential parameter σ_{ii} as well as the σ_{ii} values estimated with the formula of Cambi et al. [37].

Atom	α, Å^3 [39]	σ_{ii}, Å
Ar	1.66	3.33
H	0.67	2.68
O	0.80	2.80
N	1.10	3.02
C	1.76	3.37
F	0.56	2.56

It is worth noting that, today, there is no common approach for determining the collision diameter for molecules and clusters. The first approach is based on the assignment of effective radius for atoms that correlate with the mean radius of the outermost electronic orbitals [33,34]. Conventionally, the values of the radius are selected empirically. Note, that this methodology was applied to polyatomic Al-containing species in reference [35].

The second approach is based on the usage of fundamental physical properties of colliding particles that are mainly responsible for van der Waals intermolecular interaction. It is supposed that the linear scale of electron density of atom is roughly proportional to $\alpha^{1/3}$ [36]. So, Cambi et al. [37] used this supposition to obtain semi-empirical correlation formula connecting directly the parameter σ_{ij} with the values of the static average polarizability α_i and α_j of colliding particles. For the general case of two species i and j, the following relationship for σ_{ij} was recommended (polarizabilities are in Å^3):

$$\sigma_{ij} = 1.767\frac{\alpha_i^{1/3} + \alpha_j^{1/3}}{(\alpha_i + \alpha_j)^{0.095}}\frac{1}{\sqrt[6]{2}}\,[\text{Å}]. \tag{13}$$

However, it should be mentioned that equation (13) was proposed for atoms and small radicals and it can hardly be applied even to Al_2O_3 monomer.

The approaches mentioned above [33,35,37] do not take into account the specific spatial structure of molecules and clusters and treat them as structureless particles. In our previous study [38], the other approach for estimation of the radius of $(Al_2O_3)_n$ clusters was suggested. It was proposed that the collision diameter of particle i with identical particle is equal to the length of cube edge with a volume of a rectangular parallelepiped of minimal volume circumscribing the aggregate of the van der Waals spheres of atoms, i.e. $\sigma_{ii} = \sqrt[3]{d_x d_y d_z}$, where d_x, d_y and d_z are the dimensions of this rectangular parallelepiped. In doing so the diameters of van der Waals spheres, centred on all atoms, are calculated with the use of formula (13) on the basis of experimental values of atomic polarizability reported in reference [39] (see Tab. 1).

To validate the prediction ability of proposed method, we compared the collision diameters for a set of some stable species predicted by the approach [38] with the reliable and generally accepted data tabulated elsewhere [32,40–42]. In addition, the effective diameters σ_{ij}^{eff}

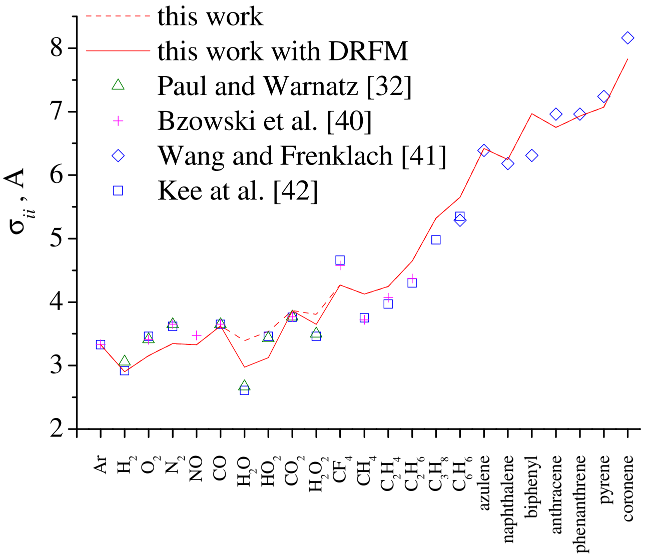

Fig. 1. The values of collision diameter σ_{ii} for various individual species i = Ar, H_2, O_2, N_2, NO, CO, H_2O, HO_2, CO_2, H_2O_2, CF_4, CH_4, C_2H_4, C_2H_6, C_3H_8, C_6H_6 and polyaromatic hydrocarbons (azulene, naphthalene, biphenyl, anthracene, phenanthrene, pyrene, coronene) determined in the present work (dotted line) as well as the effective diameters in terms of DRFM (solid lines) and the available data given in references [32,40–42] (symbols).

were also calculated in line with equation (12). The comparison of the estimated values of σ_{ij} and σ_{ij}^{eff} with the tabulated data is given in Figure 1. One can see an advance of the methodology proposed in reference [38] and applied in the present work for the adequate predictions of the collision diameters of different species (the relative mean deviation does not exceed 6%). Notable discrepancy is observed only for the σ_{ii} values for the H_2O, H_2O_2 and CF_4 molecules and for two polyaromatic hydrocarbon molecules $C_{12}H_{10}$ and $C_{24}H_{12}$. The account for the dipole-dipole and dipole-induced dipole interactions in the manner of Paul and Warnatz (DRFM) [32] makes it possible to improve the agreement between predicted and commonly accepted values of σ_{ii} for dipole molecules H_2O and H_2O_2.

Note that, when calculating the binary diffusion coefficient D_{ij}, a few combining rules for the collision diameter σ_{ij} of different molecules can be applicable. One of the combining rules, commonly used for the calculation of collision diameter, is the arithmetic mean

$$\sigma_{ij} = 0.5\left(\sigma_{ii} + \sigma_{jj}\right). \tag{14}$$

This rule is exactly valid if the interacting particles are hard spheres. More sophisticated rule of Kong [43] was proposed originally assuming LJ potential for noble gases. However, as it was found from fitting the transport properties for binary mixtures [44], both the arithmetic mean and Kong's rule overpredicts the collision diameter for the particles with considerably distinguishing sizes. This issue is essential for the cases under study, because we consider binary diffusion of rather large clusters in diatomic gases. Therefore, we used the empirical combining rule suggested by Bastien et al. [44]

$$\sigma_{ij} = 0.43\left(\sigma_{ii} + \sigma_{jj}\right) + 0.49. \tag{15}$$

This rule provides accurate values of σ_{ij} for the cases of substantially distinguishing diameters of molecules (all values in Eq. (15) are in Å).

2.3 Electric properties of clusters

In recent study [38] the main electric properties such as dipole moments and static polarizabilities for $(Al_2O_3)_n$, $n = 1\ldots4$, clusters were reported for structures optimized in terms of density functional theory (DFT) with the use of Becke three parameter hybrid functional (B3LYP) [45] combined with the correlation functional [46] with the use of 6-31+G(d) basis set. However, this method does not provide highly accurate values of electric properties [47]. Therefore, in the present work, in accordance with the recommendations [48], the following calculation procedure was applied. At first, the estimations of dipole moments μ and static polarizabilities $\langle\alpha\rangle$ were performed by using the UB3LYP/6-311+G(2d) level of theory for the geometries of cluster structures reported in reference [38]. The commonly applied notation for this kind of calculations is UB3LYP/6-311+G(2d)//UB3LYP/6-31+G(d) method. Then, the values of static isotropic polarizability $\langle\alpha\rangle$ estimated with this method were scaled by a factor of 1.11, that provides the best coincidence with the known experimental data [39] for a test set composed of 21 species (He, Ar, Ne, H, O, N, C, B, Al, Na, H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_6H_6). Note that all DFT computations were performed by using Firefly QC program package [49] which is partially based on the GAMESS(US) source code [50].

3 Results

We considered each two most stable $(Al_2O_3)_n$, $n = 1\ldots4$ isomers of each type of clusters (monomer, dimer, trimer, tetramer) identified in reference [38]. Their configurations are shown in Figure 2.

The calculated values of collision diameter σ_{ii}, isotropic polarizability $\langle\alpha\rangle$ and dipole moment μ as well as symmetry type and multiplicity for the most stable $(Al_2O_3)_n$ isomers are given in Table 2. The values of $\langle\alpha\rangle$ scaled by factor 1.11 are given also in the parentheses. One can see that the majority of the considered clusters are non-polar. Only triplet monomer of C_{2v} symmetry and singlet trimer of C_1 symmetry have substantial dipole moments. For comparison the values of $\langle\alpha\rangle$ (non-scaled and scaled) calculated in the present work for the most stable clusters are given in Figure 3. The $\langle\alpha\rangle$ value for Al_2O_3 derived by using the Clausius-Mossotti relation from the dielectric constant for sapphire (>99.9% Al_2O_3) [51] is also given there. Note, though the Clausius-Mosotti equation is

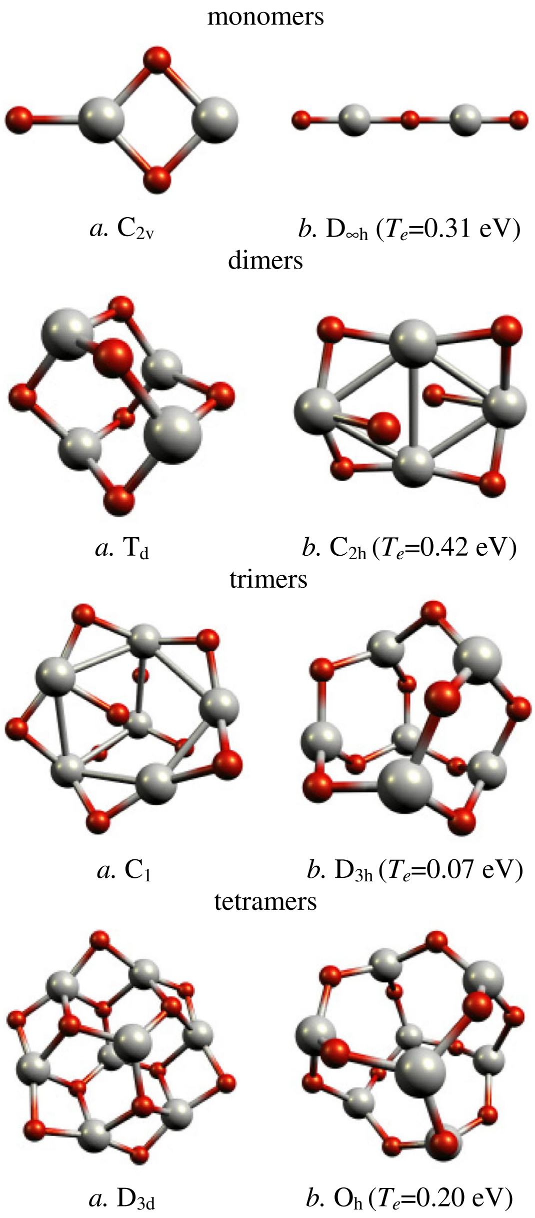

Fig. 2. Considered structures of $(Al_2O_3)_n$, $n = 1 \ldots 4$, clusters (Al and O atoms are depicted by grey and red colour). The type of symmetry and electronic energy values of isomers T_e are also indicated.

Table 2. Collision diameter and electric properties of considered $(Al_2O_3)_n$ clusters.

n	Symmetry	Multiplicity	σ_{ii}, Å	$\langle\alpha\rangle$, Å^3	μ, D
1	C_{2v}	3	5.77	8.60 (9.55)	2.47
1	$D_{\infty h}$	1	6.08	9.14 (10.15)	0.0
2	T_d	1	6.91	12.91 (14.33)	0.0
2	C_{2h}	1	6.71	12.99 (14.42)	0.0
3	C_1	1	8.02	18.15 (20.14)	1.32
3	D_{3h}	1	7.65	18.85 (20.92)	0.0
4	D_{3d}	1	8.71	24.33 (27.00)	0.02
4	O_h	1	8.20	24.87 (27.60)	0.0

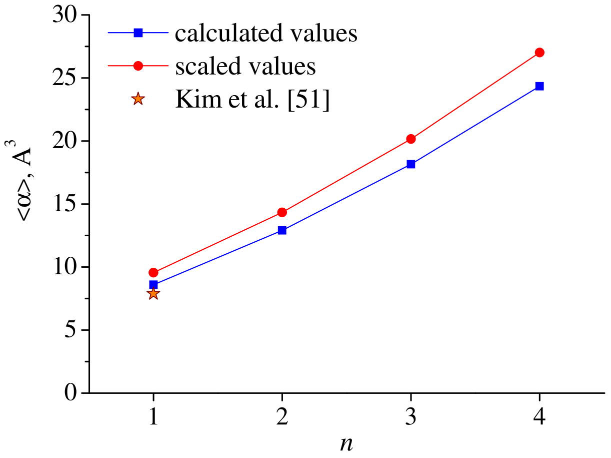

Fig. 3. The values of $\langle\alpha\rangle$ for the most stable $(Al_2O_3)_n$, $n = 1 \ldots 4$, clusters estimated in the present work as well as the $\langle\alpha\rangle$ value for Al_2O_3 derived from the dielectric constant of sapphire [51].

strictly valid only for crystals with cubic lattice, the agreement of $\langle\alpha\rangle$ values, estimated in this work for the monomer and derived from the data for sapphire [51], is rather good. In addition, one can observe from Figure 3 that the variation of polarizability of alumina clusters with increasing n number is not absolutely linear. There exists small quadratic dependence: $\langle\alpha\rangle\ (n) = 5.81 + 3.22n + 0.519n^2$.

The analogous data for cluster colliding partners considered in the present study: H_2, N_2, O_2, CO and H_2O that were calculated with the use of the methodology of this work are presented in Table 3. Comparing the predicted $\langle\alpha\rangle$ values with experimental data, one can conclude that the usage of scaling parameter of 1.11 allows one to compensate the effect of underestimation of the polarizability caused by using the limited basis set in quantum chemical computations. The coincidence of predicted dipole moments with experimental data can be also considered as acceptable.

From the plot shown in Figure 4 it also follows that the applied methodology allows us to predict binary diffusion coefficients for pairs of nonpolar-nonpolar and polar-nonpolar molecules at $T = 298$ K [52,53] with reasonable accuracy.

One of the most crucial issues important for the problem under study is the temperature dependence of diffusion coefficient for pairs of polar-nonpolar and polar-polar particles. In order to elucidate this topic we compared our predictions with the experimental data on self-diffusion coefficient for strongly polar molecule H_2O reported in the review [54] and on diffusion coefficient of slightly polar molecule CO in O_2 given in reference [53]. Figure 5 depicts the dependencies of diffusion coefficients calculated both with DRFM approach and using the additive scheme (Eq. (6)). One can see that the applied methodology predicts diffusion coefficient for polar gas in non-polar ones very well, irrespectively on the way of account for the orientation-dependent contributions. However, for the H_2O self-diffusion coefficient the DRFM

Table 3. The collision diameter and electric properties of considered bath gas molecules.

Molecule	Multiplicity $2s+1$	σ_{ii}, Å	$\langle\alpha\rangle$, Å^3, calculations	$\langle\alpha\rangle$, Å^3 scaled	$\langle\alpha\rangle$, Å^3, experiment [39]	μ, Debye, calculations	μ, Debye, experiment [39]
H_2	1	2.91	0.60	0.67	0.79	0.0	0.0
N_2	1	3.35	1.63	1.81	1.71	0.0	0.0
O_2	3	3.16	1.35	1.50	1.56	0.0	0.0
CO	1	3.63	1.84	2.05	1.95	0.06	0.11
H_2O	1	3.40	1.23	1.37	1.45	1.95	1.85

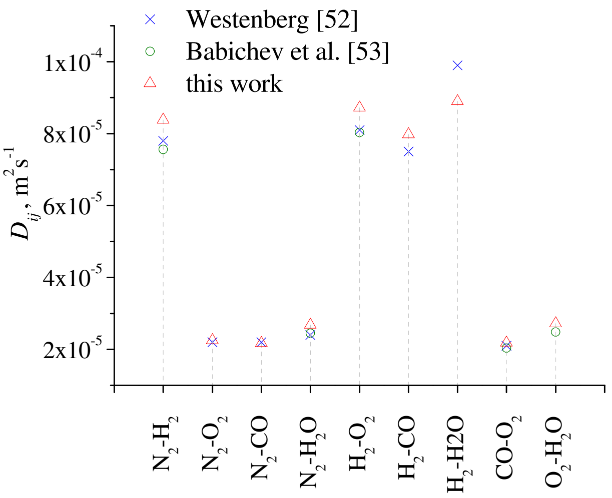

Fig. 4. Measured [52,53] and estimated binary diffusion coefficients for different pairs of bath gases considered in this work at the temperature $T = 298$ K and pressure $P = 1$ atm.

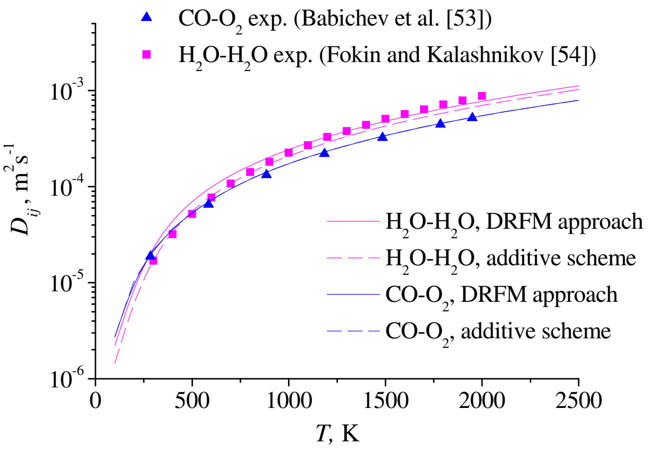

Fig. 5. Diffusion coefficients for H_2O-H_2O and CO-O_2 molecular pairs vs. temperature calculated in line with DRFM approach and using the additive scheme (Eqs. (5) and (6)) (curves) and the experimental data [53,54] at $P = 1$ atm (symbols).

approach, at high temperatures, provides a slightly better agreement of predicted D_{ij} values with measurements. Therefore, the DRFM approach was applied for the evaluation of D_{ij} values for $(Al_2O_3)_n$ clusters.

In Table 4 the dispersion potential well depths ε_{ij}^{disp} for pairs "cluster-bath gas molecule" as well as the effective potential well depth values ε_{ij}^{eff} at $T = 298$ K are summarized. One can see that, as was expected, the values of ε_{ij}^{disp} and ε_{ij}^{eff} differ only for the strongly polar molecules (H_2O) and clusters possessing the dipole moment.

It is worth noting that preliminary quantum chemical calculations of interaction potential for two Al_2O_3 monomers with the use of unrestricted second order Møller-Plesset perturbation theory (UMP2) method [55] revealed that this potential is highly attractive, and the interaction of monomers leads to the direct formation of highly stable dimer rather than van der Waals complex. That is why the collisions of Al_2O_3 monomers cannot be treated as elastic. Therefore, the procedure of the determination of self-diffusion and viscosity coefficients for the monomers is meaningless.

The binary diffusion coefficients of $(Al_2O_3)_n$ clusters at atmospheric pressure in various bath gases as well as self-diffusion coefficients for clusters with $n = 2\ldots4$ were calculated with the usage of ε_{ij}^{eff} values. The temperature-dependent diffusion coefficients for $(Al_2O_3)_n$ clusters were approximated by following formula

$$D_{ij}(T) = D_{ij}^{0}\left[\left(\frac{T}{273}\right)^{a} - b\exp\left(-c\frac{273}{T}\right)\right] \qquad (16)$$

with an accuracy not worse than ±2% over the temperature range $T = 300$–6000 K. The D_{ij}^0, a, b, and c parameters are presented in Table 5. The $D_{ij}(T)$ dependencies for $j = N_2$ (non-polar molecule gas), CO (weakly polar molecule gas) and H_2O (polar molecule with large dipole moment) as well as self-diffusion coefficients $D_{ij}(T)$ are shown in Figures 6–9.

The presented data exhibit that an account for the contributions of the second type isomer for each type of clusters (dimer, trimer, tetramer) cannot provide a substantial correction to the net diffusion coefficient, because the isomers possess similar collision diameters and polarizabilities (see Tab. 2). However, the most stable monomer ($^3C_{2v}$) has substantial dipole moment (2.47 D), whereas the singlet monomer has $D_{\infty h}$ symmetry, and its dipole moment is equal to zero. This leads to the substantial difference in their diffusion coefficients in the gas of polar molecules at low temperature due to distinguishing values of C_6^{el} term in the interaction potential responsible for the dipole-dipole interaction for these isomers. So, at low temperature ($T = 200$–300 K), for $j = H_2O$ we have $D_{ij}(^1D_{\infty h}) = (1.04 \div 1.51)\ D_{ij}(^3C_{2v})$. To a lesser extent, the difference in the diffusion coefficients, at low

Table 4. The values of dispersion potential well depth ε_{ij}^{disp} and values of ε_{ij}^{eff} calculated in terms of DRFM approach (Eq. (12)) (in parentheses) for different pairs of collision partners at $T = 298$ K.

ε_{ij}, K	Mono $^3C_{2v}$	Mono $^1D_{\infty h}$	Dimer T_d	Dimer C_{2h}	Trimer C_1	Trimer D_{3h}	Tetramer D_{3d}	Tetramer O_h
CO	95.3 (100.7)	83.4 (83.4)	83.5 (83.5)	93.3 (93.3)	69.3 (69.8)	85.0 (85.1)	67.6 (67.6)	86.8 (86.8)
H_2	42.7 (45.4)	37.0 (37.0)	35.6 (35.6)	40.0 (40.0)	28.5 (28.7)	35.3 (35.3)	27.3 (27.3)	35.5 (35.5)
H_2O	75.4 (156.6)	65.7 (82.2)	65.5 (80.2)	73.2 (89.7)	53.8 (70.5)	66.2 (81.0)	52.1 (63.7)	67.2 (82.2)
N_2	101.7 (107.2)	88.5 (88.5)	87.9 (87.9)	98.4 (98.4)	72.1 (72.5)	88.7 (88.7)	69.8 (69.8)	90.1 (90.1)
O_2	101.1 (106.2)	87.6 (87.6)	86.9 (86.9)	97.5 (97.5)	70.7 (71.1)	87.2 (87.2)	68.2 (68.2)	88.2 (88.2)
Self	–	–	78.7 (78.7)	95.0 (95.0)	65.7 (66.8)	92.4 (92.4)	71.7 (71.7)	106.7 (106.7)

Table 5. Approximation parameters for the temperature dependence for the self-diffusion coefficients D_{ii} and binary diffusion coefficients D_{ij} (in $m^2\ s^{-1}$) in various bath gases: CO, H_2, H_2O, N_2, O_2 for two structures of $(Al_2O_3)_n$, $n = 1 \ldots 4$ clusters.

Monomer $^3C_{2v}$					Monomer $^1D_{\infty h}$				
partner	D_{ij}^0, $m^2\ s^{-1}$	a	b	c	partner	D_{ij}^0, $m^2\ s^{-1}$	a	b	c
CO	9.86×10^{-6}	1.651	1.12×10^{-1}	0.2691	CO	9.45×10^{-6}	1.652	7.59×10^{-2}	0.1966
H_2	4.24×10^{-5}	1.655	1.73×10^{-2}	–0.0519	H_2	4.07×10^{-5}	1.655	9.09×10^{-3}	–0.1631
H_2O	1.32×10^{-5}	1.641	2.58×10^{-1}	0.3381	H_2O	1.23×10^{-5}	1.652	7.35×10^{-2}	0.1908
N_2	1.03×10^{-5}	1.650	1.26×10^{-1}	0.2934	N_2	9.87×10^{-6}	1.652	8.61×10^{-2}	0.2198
O_2	1.02×10^{-5}	1.651	1.24×10^{-1}	0.2897	O_2	9.75×10^{-6}	1.652	8.41×10^{-2}	0.2155
with itself	–	–			with itself	–	–		
Dimer ^1T_d					Dimer $^1C_{2h}$				
CO	7.70×10^{-6}	1.652	7.61×10^{-2}	0.1972	CO	7.86×10^{-6}	1.651	9.58×10^{-2}	0.2399
H_2	3.48×10^{-5}	1.655	7.91×10^{-3}	–0.1887	H_2	3.55×10^{-5}	1.655	1.18×10^{-2}	–0.1171
H_2O	1.02×10^{-5}	1.652	6.97×10^{-2}	0.1811	H_2O	1.04×10^{-5}	1.652	8.85×10^{-2}	0.2249
N_2	8.03×10^{-6}	1.652	8.48×10^{-2}	0.2170	N_2	8.19×10^{-6}	1.651	1.07×10^{-1}	0.2605
O_2	7.85×10^{-6}	1.652	8.28×10^{-2}	0.2126	O_2	8.01×10^{-6}	1.651	1.05×10^{-1}	0.2568
with itself	2.01×10^{-6}	1.652	6.68×10^{-2}	0.1735	with itself	2.08×10^{-6}	1.651	9.94×10^{-2}	0.2469
Trimer $^1C_1$					Trimer $^1D_{3h}$				
CO	6.46×10^{-6}	1.653	5.11×10^{-2}	0.1267	CO	6.66×10^{-6}	1.652	7.91×10^{-2}	0.2041
H_2	2.96×10^{-5}	1.656	3.31×10^{-3}	–0.3630	H_2	3.05×10^{-5}	1.655	7.73×10^{-3}	–0.1930
H_2O	8.58×10^{-6}	1.653	4.93×10^{-2}	0.0628	H_2O	8.84×10^{-6}	1.652	7.11×10^{-2}	0.1848
N_2	6.71×10^{-6}	1.653	5.58×10^{-2}	0.1418	N_2	6.93×10^{-6}	1.652	8.64×10^{-2}	0.2206
O_2	6.54×10^{-6}	1.653	5.34×10^{-2}	0.1342	O_2	6.75×10^{-6}	1.652	8.34×10^{-2}	0.2140
with itself	1.25×10^{-6}	1.653	4.61×10^{-2}	0.1065	with itself	1.31×10^{-6}	1.651	9.40×10^{-2}	0.2363
Tetramer $^1D_{3d}$					Tetramer ^1O_h				
CO	5.77×10^{-6}	1.653	4.76×10^{-2}	0.1144	CO	6.03×10^{-6}	1.652	8.26×10^{-2}	0.2122
H_2	2.66×10^{-5}	1.656	2.62×10^{-3}	–0.4138	H_2	2.78×10^{-5}	1.655	7.87×10^{-3}	–0.1898
H_2O	7.68×10^{-6}	1.653	4.14×10^{-2}	0.0909	H_2O	8.02×10^{-6}	1.652	7.35×10^{-2}	0.1909
N_2	5.99×10^{-6}	1.653	5.12×10^{-2}	0.1269	N_2	6.26×10^{-6}	1.652	8.92×10^{-2}	0.2264
O_2	5.82×10^{-6}	1.653	4.85×10^{-2}	0.1175	O_2	6.08×10^{-6}	1.652	8.54×10^{-2}	0.2183
With itself	9.08×10^{-7}	1.653	5.43×10^{-2}	0.1370	with itself	9.71×10^{-7}	1.650	1.25×10^{-1}	0.2916

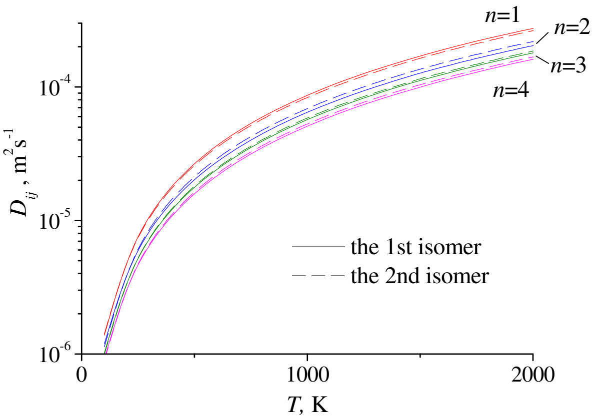

Fig. 6. Diffusion coefficients of the two energy-lowest isomers of $(Al_2O_3)_n$ $(n = 1\dots4)$ clusters with N_2.

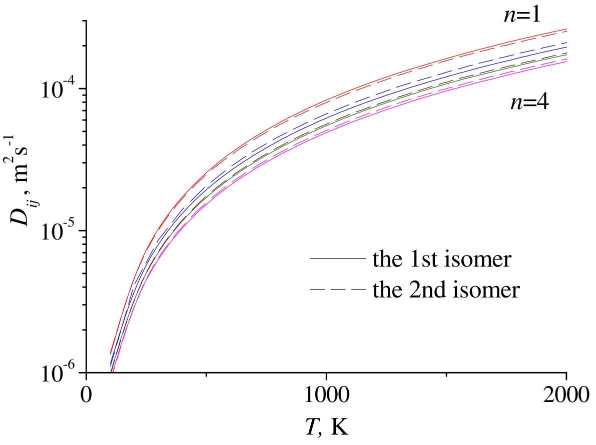

Fig. 7. Diffusion coefficients of the two energy-lowest isomers of $(Al_2O_3)_n$ clusters $(n = 1\dots4)$ with CO.

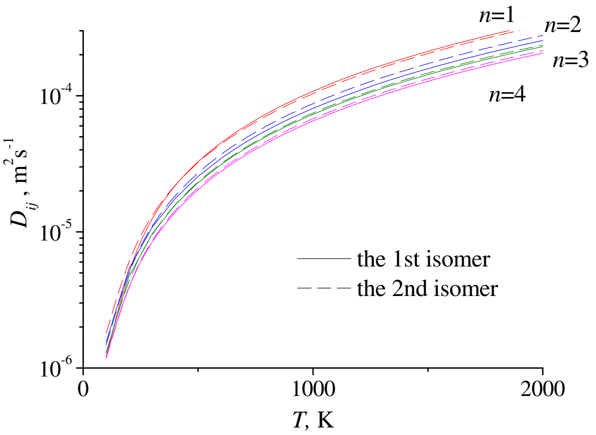

Fig. 8. Diffusion coefficients of the two energy-lowest isomers of $(Al_2O_3)_n$ clusters $(n = 1\dots4)$ with H_2O.

temperature, takes place for polar C_1 trimer and non-polar D_{3h} trimer in H_2O bath gas.

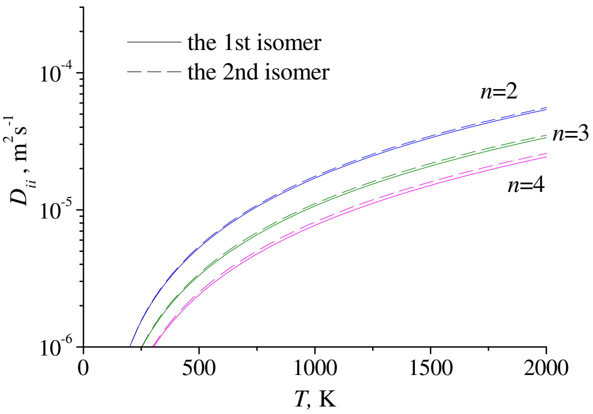

Fig. 9. Self-diffusion coefficients of the two energy-lowest isomers of $(Al_2O_3)_n$ $(n = 2\dots4)$ clusters.

4 Concluding remarks

Binary diffusion coefficients for two low-lying pairs of isomers of $(Al_2O_3)_n$ clusters $(n = 1\dots4)$ in bath gases, H_2, CO, N_2, O_2 and H_2O as well as self-diffusion coefficients for clusters with $n = 2\dots4$ were computed over a wide range of temperature using first-principle calculations and reliable interaction potential. The parameters of the potential for $(Al_2O_3)_n$ clusters interaction with H_2, CO, N_2, O_2 and H_2O molecules were calculated taking into account the dispersion, dipole-dipole and dipole-induced dipole interaction terms. Special attention was paid to the correct determination of collision diameter of colliding partners (cluster-molecule). A comparison of the computed diffusion coefficients for pairs of bath gases with experimental data, obtained at near room temperature showed an advance of applied methodology. It was revealed that the diffusion coefficients of the isomers of $(Al_2O_3)_n$ clusters differ notably only in the case when dipole moments of isomers distinguish strongly. So, the diffusion coefficients of two Al_2O_3 structures with $^3C_{2v}$ and $^1D_{\infty h}$ symmetries in water vapour can differ by a factor of 1.5 at $T = 200$–300 K.

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