THEORETICAL STUDY OF THE vdW COMPLEX Cd⋯N$_2$

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

The supermolecular CCSD(T) *ab initio* calculations of potential energy surface for the electronic ground state of van der Waals complex formed from a cadmium atom and a nitrogen molecule are presented. Our calculations indicate the bent orientation (Jacobi coordinates are r_{N-N} = 1.10 Å, R = 4.53 Å, angle θ = 62°) of the van der Waals (vdW) system with a well depth of D_e = 73.3 cm^{-1}. This well depth was shifted to the value of 76.7 cm^{-1} by systematical extension of mid-bond functions. The temperature dependences of the theoretical coefficient of diffusion were evaluated from the molecular dynamics and the Enskog–Chapman theory. The theoretical values at 273 K are compared with the available experimental data.
Keywords: Cadmium; Nitrogen molecule; Weak interaction; *Ab initio* calculations; Transport properties; Enskog–Chapman Theory; Molecular dynamics.

In the last years a lot of experimental and theoretical effort has been put to the study of elementary chemical processes and energy transfer at the microscopic level. Obtained experimental information is leading to more fundamental understanding of these processes as well as to new theoretical studies in this area. The intense interest in the interaction of N$_2$ molecule with atoms has been initiated by experimental laser "pump-and-probe" technique developed by Breckenridge group where in the first pump-and-probe experiment the N$_2$ molecule was chosen as a quencher molecule[1]. Precise studies of pressure broadening and shift of the cadmium 326.1 nm (5^1S_0-5^3P_1) intercombination line perturbed by noble gases and non-polar molecular gases performed by means of a laser-induced fluorescence method were reported in papers of Bielski and coworkers[2–5]. The quenching

cross sections correlate with the C_6 long-range forces parameter and in order to interpret the pressure broadening, shift and collision-time asymmetry data, the realistic interaction potentials should first be known. The first systematic investigation of the broadening, shift and asymetry in the Cd–N_2 mixtures was performed by Bielski et al. in recent study[6]. Neither the theoretical nor experimental potentials for Cd–N_2 complex were available, therefore they used for the interpretation of their data the approximate formula for van der Waals potential. The potential energy surface (PES) for the interaction of N_2 molecule with rare gas atoms has been theoretically studied in a number of papers[7–16]. However, the theoretical studies of the interaction of Cd atoms with diatomic molecules are very rare and we have found only two ab-initio studies of PES and spectroscopic constants for the van der Waals complex of Cd with H_2 [17,18], but none theoretical potential for Cd–N_2 complex.

The major part of the above mentioned *ab initio* studies was performed using the supermolecular (SM) approach[19] where the interaction energy is obtained as the difference between the value of the energy of the complex E_{AB} and the sum of the energies of its constituents ($E_A + E_B$)

$$E_{int} = E_{AB} - E_A - E_B .\tag{1}$$

Although the SM approach is conceptually and computationally simple, it cannot offer a detailed picture of interaction forces. The intermolecular perturbation theory (I-PT) defined as symmetry adapted perturbation theory (SAPT)[19] allows the direct calculations of electrostatic (E_{elst}), exchange-penetration (E_{exch}), dispersion (E_{disp}) and induction (E_{ind}) contributions that provide the physical interpretation of the interactions between the monomers of a complex

$$E_{int} = \sum E_{els}^{(nij)} + \sum E_{ind}^{(nij)} + \sum E_{disp}^{(nij)} + \sum E_{exch}^{(nij)} + \sum E_{other}^{(nij)} + \dots \tag{2}$$

The superscript n in Eq. (*2*) denotes the order of the perturbation V_{AB} and i (j) indicate the order of the Møller–Plesset fluctuation potential for the A (B) system.

The goal of this work is to provide a basis set superposition error (BSSE)-free characterization of Cd⋯N_2 vdW system at supermolecular CCSD(T) theoretical level. Due to the character of constituents the disper-

sion energy should be the major contribution to the correlation interaction energy. The angular dependence of this main physical contribution to interaction – the dispersion energy calculated in the frame of the SAPT is presented. Finally, on the basis of the obtained theoretical PES, a simulation of the temperature dependence of the coefficient of diffusion will be performed. The comparison of theoretical data and applied theoretical approaches with a thermodynamical experiment offers an independent (non-spectroscopic) information on the electronic ground state interaction potential.

CALCULATION DETAILS

Quantum Chemical Calculation Details

A system of Jacobi coordinates (r, R, θ) was used to describe the geometry of the studied complex. The coordinates r, R and θ represent intramolecular N–N distance, the distance from Cd to the centre of N_2 molecule and the Jacobi angle ($\theta = 0°$ in linear arrangement of N_2···Cd), respectively. The interaction energy was determined at $r = 1.10$ Å for 10 values of θ (0, 10, 20, 30, 40, 50, 60, 70, 80 and 90°) in the range of R from 3.5 to 10.0 Å.

I-PT calculations were performed by SAPT program codes[20] interfaced to the Gaussian 03 program package[21]. Gaussian 03 was also used for SM calculations. The supermolecular BSSE was determined via the counterpoise method of Boys and Bernardi[22]. The presented HF interaction energy terms were developed using dimer-centered basis sets of the constituent monomers. In the present study the relativistic small core STUTTGART RSC 1997 ECP [23] pseudopotential for Cd atom was used. For N atom the aug-cc-pVTZ basis set was used[24]. In order to improve the effects of the basis set on the quality of interaction energy calculations, we have used also the set of modified mid-bond functions [3s3p2d2f] of Tao and Pan[25] (with the exponents s,p: 0.9, 0.3, 0.1; d,f: 0.6, 0.2). These bond functions are fixed at the center of the axis defined by the mass centre of N_2 molecule and cadmium atom. The localization of the minimum on the PES was performed also without mid-bond functions using cc-pVTZ-DK basis set of Peterson et al.[26] for Cd atom and aug-cc-pVTZ basis set for N [24] atoms. Also in order to verify the quality of mid-bond functions some other calculations were performed where the existing mid-bond functions were systematically extended by s, p, d and f functions to achieve the maximal decrease of the interaction energy.

Diffusion Coefficients

Enskog–Chapman Theory

The coefficient of diffusion D_{12} for low density atomic gas can be calculated as[27]

$$D_{12} = \frac{3}{8} \frac{\sqrt{\pi k^3 T^3 (m_1 + m_2)/2 m_1 m_2}}{p \pi \sigma_{12}^2 \Omega_{12}^{(1,1)*}(T^*)} \qquad (3)$$

where m_1, m_2 are atomic weights, k is Boltzmann constant, σ is the collision diameter for low energy collisions (it is the value of the interatomic distance where the potential function equals to zero), T is the absolute temperature and T^* is the reduced temperature ($T^* = kT/D_e$, where D_e is the well depth of potential energy curve of the interaction between atom 1 and atom 2) and $\Omega^{(l,s)*}(T^*)$ is a collision integral. General formula for calculating collision integrals $\Omega^{(l,s)*}(T^*)$ in[28] is

$$\Omega^{(l,s)*}(T^*) = \frac{1}{(s+1)! \, T^{*s+2}} \int_0^\infty e^{\frac{E^*}{T^*}} E^{*s+1} \, Q^{(l)*}(E^*) \, dE^* \qquad (4)$$

where E^* is reduced kinetic energy ($E^* = E/D_e$) and $Q^{(l)*}$ are reduced cross-sections

$$Q^{(l)*}(g^*) = \frac{2}{1 - \frac{1}{2}\frac{1+(-1)^l}{1+l}} \int_0^\infty (1 - \cos^l \chi) b^* \, db^* \qquad (5)$$

with b^* being the reduced impact parameter ($b^* = b/\sigma$). The angle of deflection $\chi(E^*, b^*)$ depends on the potential function. For the calculation of the collision integral we use the computer code given in Appendix 12 of work[27] which is based on the method illustrated in[29].

In a monoatomic gas (or mixture of monoatomic gases) the resulting motion after collision of two atoms depends besides the initial motion vectors of the colliding atoms on the potential function which depends on the interatomic distance only. In a gas containing molecules consisting of two or more atoms, the motion after collision with such molecules depends on much more parameters (e.g. relative angular displacement, the phase of the rotation at the moment of the collision). In order to use the expressions

valid for monoatomic gases, the potential function has to be averaged to depend only on the distance. One possible way is to calculate the coefficients of diffusion for all angular displacements ($D_{12}(\theta)$). Consequently, the resulting coefficient of diffusion is obtained by angle averaging through whole space

$$\overline{D}_{12} = \frac{1}{4\pi} \int\limits_0^{2\pi} \int\limits_0^{\pi} D_{12}(\theta) \sin\theta \, d\theta d\phi = \int\limits_0^{\pi/2} D_{12}(\theta) \sin\theta \, d\theta . \tag{6}$$

Molecular Dynamics Simulations

Molecular dynamics represents another approach to the calculation of the diffusion coefficient. This coefficient may be obtained from the mean-square displacements of the particles in a medium according to the Einstein formula

$$D = \lim_{t \to \infty} \frac{1}{2d} \frac{1}{Nt} \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2 \tag{7}$$

where t is time, d is the dimension of space and $r_i(t)$ is the position vector of i-th particle in time t. Including all the particles of one-component medium, the coefficient of self-diffusion is obtained. To obtain the diffusion coefficient of a pair of substances, the mean-square displacements of one substance particles in the mixture of both substances need to be "measured". Depending on the concentration of the studied mixture, collisions occur between the particles of the same substance and some collisions between the particles of different substances. The obtained diffusion coefficient thus holds for the concentration of the studied mixture.

Looking on the formula (3), only the potential energy curve of the interaction between particles of the different substances is involved what implies that only the collisions between particles of different substances are significant for diffusion. When there are significant only collisions between the particles of different substances, the diffusion of the particles of one substance into the pure second substance is concerned. To comply with this fact in the molecular dynamics study, the collisions between the particles of the same substance must be eliminated. This means to have a sparse distribution of one substance particles among the other substance particles and measure the mean-square displacements of sparsely distributed particles. Usually the molecular dynamics studies are performed with a relatively

small number of molecules in a periodic box. To have a sparse distribution of one substance particles means to have only one particle of one substance among the other substance particles in the periodic box. Of course, many such boxes must be examined to have a sufficient number of molecules to evaluate the coefficient of diffusion.

For molecular dynamics calculations the TINKER program package[30] was used. In the calculations for the temperature of 273 K two series of boxes were examined – cubic boxes with 50 particles of Cd and 1 particle of N_2 with the edge length of 123.8 Å and cubic boxes with 100 particles of Cd and 1 particle of N_2 with the edge length of 155.5 Å – in order to verify that the number of particles is large enough. Similarly, the calculations for the temperature of 400, 500 and 600 K, respectively, were performed. The cubic box size was chosen to obtain the resulting pressure of 1 atm in all cases.

For the propagation of dynamics trajectories the Beeman integration algorithm[31] was used. Prior to the molecular dynamics study the system was thermostatized using Berendsen thermostat[32] for the period of 300 ps or more to realize few collisions between N_2 and Cd. The thermostatized systems of particles were used in the main molecular dynamics study. This study involved 50 boxes with random initial conditions for each temperature. In these calculations the systems were left to develop freely (i.e., the thermostat was turned off) for the period of 6 000 ps. Time step was 1.5 fs, the total number of time steps for each periodic box was 4 000 000.

RESULTS AND DISCUSSION

Features of the PES

The calculated potential energy points were fitted to the following general functional form

$$V(R,\theta) = \sum_{\lambda=0}^{3} \sum_{k=1}^{6} C_{2\lambda,k} \left[\left(1 - e^{-a(R-R_0)} \right)^k - 1 \right] P_{2\lambda}(\cos\theta) . \tag{8}$$

This functional form assures the angle independence of the interaction energy at infinite values of R with the zero value of interaction energy. The symbols $P_{2\lambda}$ denote Legendre polynomials.

Points in the repulsive region with interaction energy greater than 300 cm^{-1} were excluded and the remaining 459 points were used in the fit. The obtained results (residual sum of squares and other parameters) were al-

most the same in the wide range of the values of non-linear parameter R_0. The obtained parameters of the fit (for the value of non-linear parameter R_0 = 4.7 Å) are presented in Table I. The residual sum of squares is 1.43 cm^{-2} (standard deviation of 0.06 cm^{-1}), the average absolute deviation of the fit is 0.04 cm^{-1} and the maximum absolute deviation is 0.34 cm^{-1}. Of course, the maximal deviation appears in the repulsive region. In the region of negative energies, the maximal deviation is under 0.2 cm^{-1}. Some parameters did not improve the quality of the fit. Their values were fixed at 0 cm^{-1}.

Based on the fitted function, the positions of the vdW minimum and saddle points were determined. The obtained surface (obtained from the fit) reveals a saddle point in a linear arrangement (θ = 0°) at R = 4.97 Å with the interaction energy of –58.4 cm^{-1} and a shallow minimum in the range of θ from 60 to 90° (Fig. 1). The absolute minimum appears to be at θ = 62° and R = 4.53 Å. The interaction energy is –73.3 cm^{-1}. In the T-shaped geometry, the second saddle point at R = 4.48 Å with the interaction energy of –70.8 cm^{-1} occurs. In order to verify the position of the minimum at θ = 62°, additional calculations without mid-bond functions were performed using the larger basis set of Peterson et al.[26] for Cd atom. These calculations also confirmed the localization of minima around 60°. The interaction energy of –61.5 cm^{-1} was obtained at θ = 60° and R = 4.58 Å comparing with –58.1 cm^{-1} at θ = 90° and R = 4.52 Å. The systematical extension of mid-bond functions (new mid-bond functions with exponents s,p: 0.2 and d,f: 0.3 were added to the existing basis set with mid-bond functions) does not disconfirm the localization of the minimum at θ = 62° (Fig. 2).

TABLE I
Linear coefficients $C_{2\lambda,k}$ of the function (7). Non-linear coefficients are a = 0.69100569 Å^{-1} and R_0 = 4.7 Å

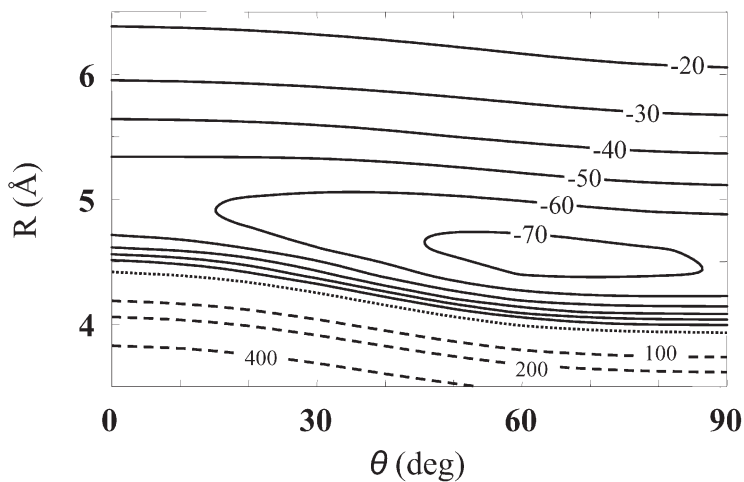| k	2λ			
	0	2	4	6
1	16.702485	–88.138928	–42.152174	–3.7712857
2	180.80796	174.30246	56.604744	4.7131126
3	–152.14834	–96.190951	–26.79645	–2.0185684
4	9.2615183	–9.1288831	0	0
5	8.415716	4.9470376	0	0
6	4.3278732	7.8584007	1.5545075	0

Fɪɢ. 1
Contour plot of the calculated interaction potential (r = 1.10 Å) at the supermolecular CCSD(T) level of theory. All energies are in cm^{-1}

Fɪɢ. 2
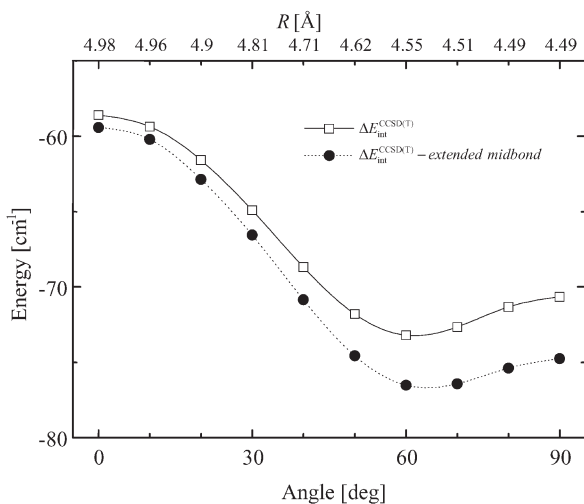Angular dependence of the CCSD(T) interaction energies $E_{int}^{CCSD(T)}$ with non-extended (□) and extended (●) set of mid-bond functions along the bottom of PES valley. Variation of the Jacobi distance R with the Jacobi angle θ along the PES valley is labeled on the top axis

Similar results were obtained also for Hg···N$_2$ complex[33]. The absolute minimum was determined to be at θ = 64.4° and R = 4.38 Å with the interaction energy of –89.0 cm^{-1}. In the T-shaped geometry, the second saddle point with the interaction energy of –86.6 cm^{-1} was localized at R = 4.34 Å. The localization of the minimum around 65° was also confirmed by additional calculations without mid-bond functions using the larger basis set of Peterson et al.[26] for Hg atom.

The dominant part of the interaction correlation energy naturally originates from the dispersion energy. The dispersion energy term $E_{\mathrm{disp}}^{(2)}$ covers very well the correlation energy and has same angular dependence as $E_{\mathrm{disp}}^{\mathrm{CCSD(T)}}$ except a shift of ca. 30 cm^{-1} in energies in the angular cross-section routed through the bottom of PES valley (Fig. 3).

The obtained theoretical geometries, interaction energies and Morse oscillator approach frequencies for the vdW structure are summarized in Table II. Table II also contains our previous results for Hg···N$_2$ [33].

The quality of the Morse oscillator approach frequencies were examined by comparison with the two-dimensional solution of vibrational Schrödinger equation obtained by finite element method (FEM) approach. Following approximations were involved – it was assumed no rotation, and due to the
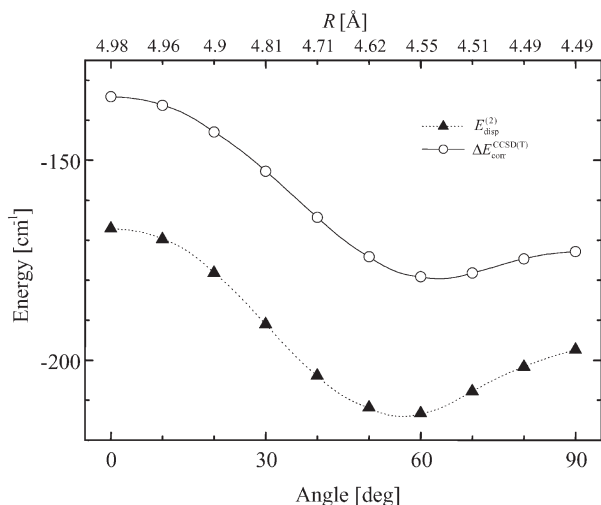

F$_{IG}$. 3

Angular dependence of the supermolecular CCSD(T) correlation interaction energy $E_{\mathrm{corr}}^{\mathrm{CCSD(T)}}$ (○) and the SAPT dispersion energy $E_{\mathrm{disp}}^{(2)}$ (▲) along the bottom of PES valley. Variation of the Jacobi distance R with the Jacobi angle θ along the PES valley is labeled on the top axis

mass difference was the position of Cd atom considered as fixed within the bending motion with regard to its small variations compared to N_2 motion (confirmed by molecular dynamics simulations). The two-dimensional vibrational Schrödinger equation has the form

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}\right)\Psi + V(X,Y)\Psi = E_{u,v}\Psi \tag{9}$$

where $\mu = m_{Cd}2m_N/(m_{Cd} + 2m_N)$ and coordinates X, Y are related with Jacobi coordinates R, θ according equations $X = R\cos\theta$ and $Y = R\sin\theta$. The quantum number u is bending quantum number and v is stretching quantum number.

At solving the two-dimensional vibrational Schrödinger equation several boundary conditions were used in order to find out if previous boundary conditions were satisfactory. The smallest value of R at which the wave function is equal to zero was varied from 3 to 1 Å. The largest value of R at which the wave function is equal to zero was varied from 10 to 15 Å. Also several meshes were used – from the meshes of uniform density in the whole region (from the coarse one to the finest one) to the adaptive meshes with very fine density in the region of lowest interaction energies and coarser density in the repulsive region and at the large distances. The number of mesh triangles was varying from 10 000 to 30 000. The vibrational energy levels up to the energy level ($u = 0$, $v = 2$) are in Table III.

TABLE II
The equilibrium structure, interaction energy and Morse oscillator approach vibrational frequencies obtained from the analytical fit (see Eq. (6))

Minimum	Cd···N_2	Hg···N_2
r (Å)	1.10	1.103
R (Å)	4.53	4.38
θ (deg)	62	65
E_{int} (cm^{-1})	–73.3	–93
ω_e (cm^{-1})	18.3	20
$\omega_e x_e$ (cm^{-1})	1.14	1.1

Vibrational energy levels (E in cm^{-1}). The wavefunctions denoted as u = 12 + 1, 13 + 1, ... have the same number of nodal planes as the wavefunctions denoted as u = 13, 14, ..., respectively, but they have nodal plane at the barrier (θ = 0 and 180°) while wavefunctions denoted as u = 13, 14, ... have non-zero values at the barier. Bending with sufficiently high bending kinetic energy can pass through the barrier – internal rotation may occur

$E_{u,v}$ (v = 0, u = 0) −63.32		$E_{u,v}$ (v = 1, u = 0) −47.18		$E_{u,v}$ (v = 2, u = 0) −33.34	
v = 0		v = 0		v = 1	
u	$E_{u,v}$	u	$E_{u,v}$	u	$E_{u,v}$
0	−63.32	17	−48.13	0	−47.18
1	−63.26	17+1	−47.07	1	−47.03
2	−61.91	18	−47.06	2	−45.90
3	−61.40	19	−45.90	3	−45.38
4	−60.38	18+1	−45.89	4	−44.43
5	−59.38	20	−44.65	5	−43.49
6	−58.30	19+1	−44.63	6	−42.48
7	−57.18	21	−43.31	7	−41.42
8	−56.06	20+1	−43.30	8	−40.37
9	−54.96	22	−41.91	9	−39.37
10	−53.88	21+1	−41.87	10	−38.43
11	−52.86	23	−40.40	11	−37.58
12	−51.92	22+1	−40.39	11+1	−37.54
12+1	−51.89	23+1	−38.85	12	−36.82
13	−51.09	24	−38.80	12+1	−36.73
13+1	−50.96	25	−37.19	13	−36.19
14	−50.44	24+1	−37.16	13+1	−35.92
14+1	−50.06	25+1	−35.47	14	−35.63
15	−49.83	26	−35.44	14+1	−35.08
15+1	−49.14			15	−34.98
16	−49.08				
16+1	−48.15				

The quality of the Morse oscillator approach was compared to the FEM solution. Energy levels of Morse oscillator are

$$E_v = \hbar\omega_e \left(v + \tfrac{1}{2}\right) - \hbar\omega_e x_e \left(v + \tfrac{1}{2}\right)^2 . \tag{10}$$

For the transitions $v = 0 \rightarrow v = 1$ and $v = 1 \rightarrow v = 2$, the energy differences of 16.0 and 13.7 cm^{-1} are obtained using the values of ω_e and $\omega_e x_e$ from Table II. The corresponding energy differences from the FEM two-dimensional solution are 16.1 and 13.8 cm^{-1}, respectively. The deviation is only of 0.1 cm^{-1}.

Diffusion Coefficients Simulations

Based on the PES fitted function and the Eqs (*3*)–(*6*), the coefficients of diffusion were calculated. In the applied model, the nitrogen molecule was considered rigid during the collisions, its geometry was fixed in the equilibrium geometry ($r = 1.10$ Å). The temperature dependence of the coefficients of diffusion $D_{12}(\theta)$ is presented in the inset of Fig. 4. The obtained curves have sigmoid character and they reflect the shape of PES. The minima oc-
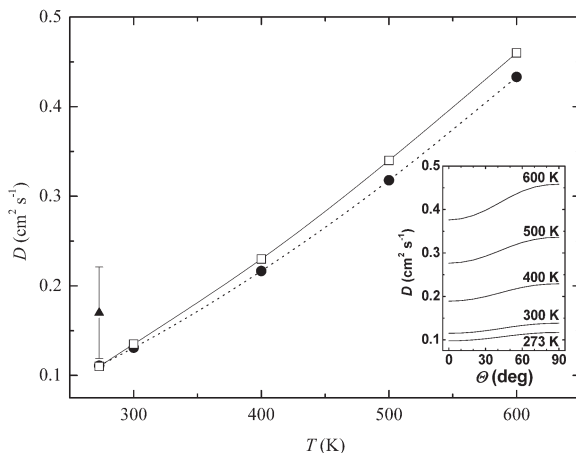

Fig. 4

The temperature dependence of the averaged diffusion coefficient obtained from the simplified model based on the Chapman–Enskog theory (●) and the molecular dynamics (□). The available experimental value with its error[37] of 30% is indicated by a triangle symbol. Inset: The temperature dependence of the diffusion coefficients for fixed angles θ from the Chapman–Enskog model

cur for linear conformations while the maxima are indicated for perpendicular arrangements. The temperature increase leads to larger differences between the largest and smallest values (for T = 300 K it is 0.023 cm^2 s^{-1} and for T = 700 K it is 0.107 cm^2 s^{-1}) as well as to higher absolute magnitudes. The coefficient of diffusion $\bar{D}_{12}$ averaged over the whole space angle increases with temperature (see Fig. 4) and is proportional to $T^{1.725}$.

In our previous work[33] we have compared the diffusion coefficient for Hg···N$_2$ (0.11 cm^2 s^{-1}, proportional to $T^{1.73}$) obtained from a simplified model based on Chapman–Enskog theory only with the work of Spier[34]. The difference was of 15%. Comparing with the values of Gardner et al.[35] (0.1252 cm^2 s^{-1}, diffusion coefficient proportional to $T^{1.761}$) and Massman[36] (0.1211 cm^2 s^{-1}, diffusion coefficient proportional to $T^{1.81}$) the agreement is better. This agreement confirms that despite the simplicity of this model the results are reliable.

In order to verify the quality of the simplified model (Eq. (6)) based on the Enskog–Chapman theory and to obtain more realistic results for the diffusion coefficient from the calculated potential function, a molecular dynamics study was performed. The obtained potential function (8) was incorporated into TINKER program package and used as the potential for the interaction between Cd and N$_2$. When calculations with vapors of cadmium at the pressure of 1 atm and temperature of 273 K are performed, real potential function describing the interaction between Cd atoms can not be used due to the formation of the aggregates of Cd atoms. Because the collisions between Cd atoms are of no interest, an arbitrary potential function can be used even the ideal gas model. The results for diffusion coefficient from molecular dynamics study are depicted in Fig. 4. They are in good agreement with the simplified model based Champan–Enskog theory.

In the case of the lowest investigated temperature T = 273 K, an experimental value is available. The comparison of the theoretical value for T = 273 K (0.11 cm^2 s^{-1}) with the available experimental value[34] of 0.17 cm^2 s^{-1} indicates the difference of 35%. It should be mentioned that the experimental value of 0.17 cm^2 s^{-1} for Cd and N$_2$ measurement was obtained by the technique where the metal is evaporated into the laminar flow of gas. As was discussed in the work of Arefev et al.[37], this technique has the error over 30% due to the aggregation of metal atoms and condensation effects occurring during the measurements because of the oversaturation of cadmium vapors. Another deviation may result from the method of the observation of the concentration profile of Cd vapours. The emitted radiation of excited atoms was measured and the interaction potential of an excited

atom differs from the potential of a ground state atom. Thus our theoretical results might be within the determined experimental error.

CONCLUSIONS

The three-dimensional *ab initio* potential energy surface for the interaction of a cadmium atom with a nitrogen molecule was evaluated at the CCSD(T) level including BSSE-correction. Very shallow minimum occurs for the bent structure. The PES saddle points are obtained for linear and perpendicular orientations. The importance of the attractive dispersion forces for the stabilization of the studied vdW system was analyzed – the dispersion energy covers very well the correlation energy. Two models were used for the simulation of a diffusion coefficient. In these models the previously obtained BSSE-free PES was used to describe the interaction between N_2 and Cd. The theoretical coefficient of diffusion corresponds to the experimental value with respect to the experimental error.

REFERENCES

1. Breckenridge W. H., Kim Malmin O., Nikolai W. L., Oba D.: *Chem. Phys. Lett.* **1978**, *59*, 38.
2. Bielski A., Ciurylo J., Domyslawska J., Lisak D., Traviński R. S., Szudy J.: *Phys. Rev. A* **2000**, *62*, 032511.
3. Traviński R. S., Bielski A., Lisak D.: *Acta Phys. Pol. A* **2001**, *99*, 243.
4. Bielski A., Lisak D., Traviński R. S.: *Eur. Phys. J. D* **2001**, *14*, 27.
5. Bielski A., Ciurylo J., Domyslawska J., Lisak D., Traviński R. S., Wolnikowski J.: *Acta Phys. Pol. A* **2000, *97***, 1003.
6. Bielski A., Lisak D., Traviński R. S., Szudy J.: *Eur. Phys. J. D* **2003**, *23*, 217.
7. Dham A. K., McCourt F. R. W., Dickinson A. S.: *J. Chem. Phys.* **2007**, *127*, 054302.
8. Stoecklin T., Voronin A., Dham A. K., Stoker J. S. F., McCourt F. R. W.: *Mol. Phys.* **2008**, *106*, 75.
9. Munteanu C. R., Cacheiro J. L., Fernandez B.: *J. Chem. Phys.* **2004**, *120*, 9104.
10. Patel K., Butler P. R., Ellis A. M., Wheeler M. D.: *J. Chem. Phys.* **2003**, *119*, 909.
11. Beneventi L., Casavecchia P., Volpi G. G., Wong C. C. K., McCourt F. R. W.: *J. Chem. Phys.* **1993**, *98*, 7926.
12. Czuchaj E.: *Chem. Phys.* **1999**, *248*, 1.
13. Fernandez B., Koch H., Makarewicz J.: *J. Chem. Phys.* **1999**, *110*, 8525.
14. Munteanu C. R., Cacheiro J. L., Fernandez B.: *J. Chem. Phys.* **2004**, *121*, 10419.

15. Zhu J., Lu Y. P., Chen X. R., Cheng Y.: *Eur. Phys. J. D* **2005**, *33*, 43.
16. Dham A. K., Meath W. J., Jechow J. W., McCourt F. R. W.: *J. Chem. Phys.* **2006**, *124*, 034308.
17. Boatz J. A., Gutowski M., Simons J.: *J. Chem. Phys.* **1992**, *96*, 6555.
18. Ramirezsolis A., Castillo S.: *J. Chem. Phys.* **1994**, *100*, 8251.
19. Chałasiński G., Szczęśniak M. M.: *Chem. Rev.* **1994**, *94*, 1723.
20. Jeziorski B., Moszyński R., Ratkiewicz A., Rybak S., Szalewicz K., Williams H. L.: *SAPT: A Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interaction Energies*. Clementi V. (Ed.) in: *METECC-94 (Methods and Techniques in Computational Chemistry)*, Vol B. STEF, Cagliari 1993.
21. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Gonzalez C., Pople J. A.: *Gaussian 03*, C.02. Gaussian, Inc., Pittsburgh (PA) 2003.
22. Boys S. F., Bernardi F.: *Mol. Phys.* **1970**, *19*, 553.
23. Küchle W., Dolg M., Stoll H., Preuss H.: *Mol. Phys.* **1991**, *74*, 1245.
24. Kendall R. A., Dunning Jr. T. H., Harrison R. J.: *J. Chem. Phys.* **1992**, *96*, 6769.
25. Tao F.-M., Pan Y.-K.: *J. Chem. Phys.* **1992**, *97*, 4989.
26. Peterson K. A., Puzzarini C.: *Theor. Chem. Acc.* **2005**, *114*, 283.
27. Maitland G. C., Rigby M., Smith E. B., Wakeham W. A.: *Intermolecular Forces*. Clarrendon Press, Oxford 1981.
28. Hirschfelder J. O., Curtiss C. F., Bird R. B.: *Molecular Theory of Gases and Liquids*, Chap. 6. John Wiley & Sons, New York 1954.
29. Barker J. A., Fock W., Smith F.: *Phys. Fluids* **1964**, *7*, 897.
30. a) Ren P., Ponder J. W.: *J. Phys. Chem. B* **2003**, *107*, 5933; b) Ren P., Ponder J. W.: *J. Comput. Chem.* **2002**, *23*, 1497; c) Pappu R. V., Hart R. K., Ponder J. W.: *J. Phys. Chem. B* **1998**, *102*, 9725; d) Hodsdon M. E., Ponder J. W., Cistola D. P.: *J. Mol. Biol.* **1996**, *264*, 585; e) Kundrot C. E., Ponder J. W., Richards F. M.: *J. Comput. Chem.* **1991**, *12*, 402; f) Ponder J. W., Richards F. M.: *J. Comput. Chem.* **1987**, *8*, 1016.
31. Beeman D.: *J. Comput. Phys.* **1976**, *20*, 130.
32. Berendsen H. J. C., Postma J. P. M., van Gunsteren W. F., DiNola A., Haak J. R.: *J. Chem. Phys.* **1984**, *81*, 3684.
33. Ilčin M., Lukeš V., Bučinský L., Laurinc V., Biskupič S.: *Int. J. Quantum Chem.* **2008**, *108*, doi: 10.1002/qua.21744.
34. Spier J. L.: *Physica* **1940**, *7*, 381.
35. Gardner P. J., Pang P., Preston S. R.: *J. Chem. Eng. Data* **1991**, *36*, 265.
36. Massman W. J.: *Atmos. Environ.* **1999**, *33*, 453.
37. Arefev K. M., Remarchuk B. F., Guseva M. A.: *J. Eng. Phys. Thermophys.* **1982**, *42*, 621.