

DETERMINATION OF THE MASS DIFFUSION COEFFICIENT OF H₂O DILUTED IN N₂ USING CLASSICAL MOLECULAR DYNAMIC SIMULATION

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Abstract. In this work, the auto-correlation function of the center of mass velocity has been used to deduce the mass diffusion coefficient (D) of water diluted in nitrogen using the Classical Molecular Dynamics Simulations (CMDS). The calculations have been performed at room temperature (296 K) for different mixtures of H₂O in N₂ and $2 \cdot 10^7$ molecules from a five-sites potential. The results show that the auto-correlation functions expected exponential decay behavior [i.e. $\Phi_{\vec{v}} = \exp(-\frac{t}{\tau_{\vec{v}}})$] and from the decay times $\tau_{\vec{v}}$, the mass diffusion coefficient and the velocity changing collisions frequency have been determined. The comparison between the CMDS results and experimental results are presented and discussed.

Keywords: water vapor, mass diffusion coefficient, velocity changing collisions.

1. Introduction

Water vapor is the most abundant greenhouse gas in the atmosphere, it is not considered to have a direct contribution to the anthropogenic increase of the greenhouse effect because human activities have only a small direct influence on atmospheric concentrations of water vapor. However, the increase of Earth's temperature causes other effects, one of them being the increase in the amount of water vapor in the atmosphere. Its concentration in the atmosphere increases when the temperature rises. Thus, water vapor plays an important role in climatology, meteorology, as the largest greenhouse gas. Indeed, water vapor and clouds provide about 80% of the current greenhouse effect [1].

For remote sensing activities to retrieve the greenhouse gas ratios, the quality of inversion depends on the theoretical model describing the spectral profile of the molecular absorption transition. To increase the accuracy in remote sensing activities, in 2014, the Hartmann-Tran profile (HTp) [2-4] that enables a very accurate description of the shapes of absorption lines was proposed for high resolution spectroscopy. This model takes into account several refined processes contributing to the line shape:

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the Dicke narrowing effect, speed dependences of collisional parameters and the correlation between velocity and rotational-states changes collisions. Comparisons with laboratory spectra have shown that the HTP enables a description of observed line shapes with an accuracy of a few 0.1% [5, 6].

Before the HTP can be used for remote sensing, the spectroscopic database must be completed with the relevant parameters. Even when limited to key species (eg. water vapor, carbon dioxide, methane) and regions (eg. those retained for the remote sensing of greenhouse gases) this is a huge task which cannot be filled rapidly by new laboratory measurements only.

For the Dicke narrowing effect [7], the velocity changes are characterized by an empirical parameter called the velocity changing collisions frequency ν_{vc} . On the other hand, this parameter can be predicted from the mass diffusion coefficient by the expression as follows [8]:

$$\nu_{vc} = \frac{k_B T}{2\pi c m D}, \quad (1)$$

where m is the molecular mass of the active molecule, D is the mass diffusion coefficient, k_B is the Boltzmann's constant, and c is the speed of light in the vacuum.

Therefore, this work is devoted to predictions of the mass diffusion coefficient D of water vapor infinitely diluted in nitrogen and also the velocity changing frequency by collisions using the CMDS.

2. Content

2.1. Classical Molecular Dynamics Simulations and the used potential

Classical molecular dynamics simulations have been performed at room temperature (296 K) for six mixtures of H_2O diluted in N_2 , with mixing ratio 5%, 10%, 15%, 20%, 25%, and 30% of H_2O . In the modeling of a complex system using methods based on the laws of classical mechanics, the used potential plays a decisive role because it determines the quality of all the calculation results. For each mixture, a total number of 2×10^7 molecules have been considered. They were divided into 500 cubic boxes and each contains 40000 molecules. The size of each box is determined using the perfect gas law from the number of molecules, temperature, and pressure. During CMDS, the velocity of the active molecule (H_2O) is computed for each time step. The autocorrelation function of the center of mass velocity is then obtained from

$$\Phi_{\vec{v}}(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle = \frac{1}{N} \sum_{i=1}^N \vec{v}_i(t) \cdot \vec{v}_i(0), \quad (2)$$

where N is the total number of molecules in the system. In statistical mechanics, this quantity decreases against the time, or the molecules forget their initial velocity. According to Boltzmann's statistics

$$\Phi_{\vec{v}}(t=0) = \langle v^2 \rangle = \frac{3}{2} \tilde{v}^2 \text{ and } \Phi_{\vec{v}}(t \rightarrow \infty) = 0, \quad (3)$$

where $\tilde{v} = \sqrt{\frac{2k_B T}{m}}$ is the most probable speed. The autocorrelation functions of the center of mass velocity can thus be written as the following analytic expressions [8, 9]

$$\Phi_{\tilde{v}}(t) = \frac{3}{2} \tilde{v}^2 \exp\left(-\frac{t}{\tau_{\tilde{v}}}\right), \quad (4)$$

where $\tau_{\tilde{v}}$ is the decay time constant characterizing the evolutions of the autocorrelation functions $\Phi_{\tilde{v}}(t)$. Note that the mass diffusion coefficient is defined as [10, 11]

$$D = \frac{\tau_{\tilde{v}} k_B T}{m}, \quad (5)$$

where k_B , T , and m are the Boltzmann constant, the temperature and the mass of the molecule, respectively. In this study, the mass diffusion coefficient D , and hence the velocity changing collisions frequency ν_{VC} are deduced from the decay time constant using expressions (1) and (5).

In our previous paper [8], we have used the site-site potential for the system H₂O in N₂ with 8 sites for H₂O molecule. This potential requires a very high-cost time, 5 five sites for both H₂O and N₂ were then proposed to use in this work. This point reduced the calculation time. For H₂O-H₂O interaction we used the intermolecular potential SAPT-5s detailed in [12]. Potential is the sum of three components

$$U = \sum_{a \in A, b \in B} \left\{ f_1(\delta_{ab}^{ab}, R_{ab}) \frac{q_a q_b}{R_{ab}} + g^{ab}(R_{ab}) e^{\alpha_{ab} - \beta_{ab} R_{ab}} + \sum_{n=6,8,10} f_n(\delta_{ab}^{ab}, R_{ab}) \frac{C_n^{ab}}{(R_{ab})^n} \right\}, \quad (6)$$

where the sum applies to all the sites a(b) of the molecule A(B). The first term describes the Coulombic contribution between sites using the function of Tang-Toennies [13]

$$f_n(\delta, R) = 1 - e^{\delta R} \sum_{m=0}^n \frac{(\delta R)^m}{m!} \quad (7)$$

The second term describes the part associated with a short distance. It varies exponentially with the separation R_{ab} . The function $g(R)$ is given by

$$g(R) = \kappa \left(1 + \sum_{m=1}^3 a_m R^m \right), \quad (8)$$

where κ is an appropriate unit of energy. The third term describes the induction and dispersion energies. The parameters of SATP-5s were determined and are presented in [12].

In order to present the N₂-N₂ interaction, we used a 5-site model. This model takes into account an electrostatic contribution and Lennard-Jonnes form whose parameters atom-atom contribution given by [14]

$$U = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\}, \quad (9)$$

where ϵ_{ij} , σ_{ij} are parameters of the interaction of the site i of the molecule A and the site j of the molecule B and r_{ij} is the distance between these sites. The charges and the geometry of each monomer and the Lennard-Jones potential parameters are given in [14].

For the $\text{H}_2\text{O}-\text{N}_2$ interaction, the used potential contains two terms based on 5 sites for both molecules. The first term is the Coulombic contribution from the charges and the geometry of each site given by [14] and [12]. The second term is the Lennard-Jones potential whose parameters are given by [15].

2.2. Results and discussion

Table 1. The time constants $\tau_{\bar{v}}$ at 296 K deduced for H_2O in the different $\text{H}_2\text{O}-\text{N}_2$ mixtures

Mixing ratio of H_2O	$\tau_{\bar{v}}$ (ps) for 0.4 amagat	$\tau_{\bar{v}}$ (ps) for 1 amagat
0.05	562.333	224.933
0.10	538.363	215.345
0.15	515.332	206.133
0.20	497.071	198.829
0.25	478.146	191.258
0.30	461.269	184.508

Figure 1 shows the autocorrelation function of the center-of-mass velocity [eq. 2] obtained from CMDS for H_2O diluted in N_2 for all the six considered mixtures. The results show that this correlation function decays exponentially against the time following eq. (4). Time constants of these decays are then deduced from exponential fit and listed in Table 1 for all considered mixing ratios. Note that, our simulations are performed for a density of 0.4 amagat, the time constants are converted to 1 amagat for clearly and shown in the last column in Table 1.

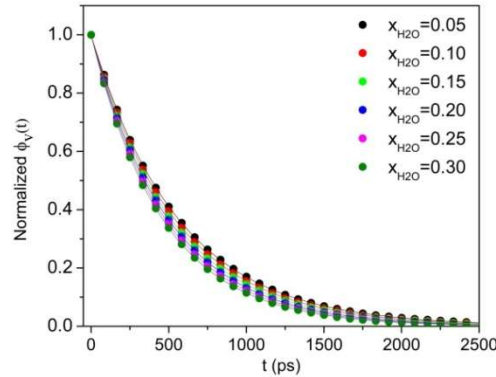


Figure 1. Room temperature normalized auto-correlation functions of the center-of-mass velocity obtained from CMDS for H_2O diluted in N_2 at six considered mixing ratios of $\text{H}_2\text{O}/\text{N}_2$. All calculated points have not been plotted and the corresponding exponential fits are plotted by continuous lines

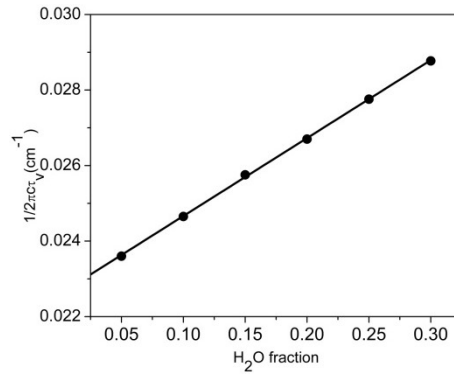


Figure 2. $\frac{1}{2\pi c\tau_v}$ as a function of the H₂O mole fraction at room temperature and for 1 amagat

If we consider that intermolecular collisions are essentially binary at the considered densities, τ_v must be proportional to $1/n$, with n the total density of the mixture. In the case of H₂O diluted in N₂, $1/\tau_v$ thus depends linearly on its concentration. This result is presented in Figure 2 where the values of $\frac{1}{2\pi c\tau_v}$ are plotted against the H₂O mole fraction. The linear fit gives a regression coefficient of $R^2 \sim 0.99964$, we can conclude that $\frac{1}{2\pi c\tau_v}$ of water vapor diluted in nitrogen versus linearly with the H₂O mole fraction. The intercept at zero concentration leads to the value of $0.02260 \pm 0.0004 \text{ cm}^{-1}$, yielding $\tau_v = 234.9 \pm 0.3 \text{ ps}$ at 1 amagat for H₂O infinitely diluted in nitrogen.

The corresponding diffusion coefficient D deduced from the value of τ_v is of $0.321 \pm 0.001 \text{ cm}^2 \cdot \text{s}^{-1}$ at 1 amagat. The mass diffusion coefficient is converted for 1 atm and 296 K using the following expression [16]

$$D = D_0 \left(\frac{p_0}{p} \right) \left(\frac{T}{T_0} \right)^{1.81} \quad (10)$$

where $p_0 = 1 \text{ atm}$ and $T_0 = 273.15 \text{ K}$. The value of D_0 , equivalent to the diffusion coefficient at 273.15 K and 1 atm pressure. The value of D and the corresponding velocity changing collisions frequency are listed in Table 2.

Table 2. The diffusion coefficients D and the velocity changing collisions frequency ν_{vc} deduced from our CMDS for pure H₂O infinitively diluted in N₂ at 1 atm and 296 K

D (cm ² .s ⁻¹) this work	D (cm ² .s ⁻¹) other work	ν_{vc} (cm ⁻¹) this work	ν_{vc} (cm ⁻¹) other work
0.371 ± 0.001	0.288 (ref. [17])	0.0195 ± 0.0001	0.0248 ± 0.0033 (ref. [18])
	0.340 [8]		0.022-0.033 [19]

As seen in Table 2, the velocity changing collisions frequency (the narrowing parameter for Dicke narrowing effect) values deduced from our CMDS is in qualitative agreement with those deduced from the fit of the absorption spectra of water vapor diluted in nitrogen [18, 19]. Comparison with our previous study [8] where we used a form 8 sites to model water vapor molecule shows an excellent agreement, however, the present 5 sites require a lower time cost.

3. Conclusions

The auto-correlation function of the center-of-mass velocity of H₂O diluted in N₂ was calculated at room temperature (296K) for different H₂O-N₂ molar mixtures (5%, 10%, 15%, 20% and 30%). The results show the expected exponential decay of the auto-correlation function against the time for all considered molar fractions. Using exponential fit, the corresponding decay time constants were deduced and the mass diffusion coefficient and the velocity changing collisions frequency for H₂O infinity diluted in N₂ have been predicted. Considered good agreements between our predictions and corresponding values from other sources demonstrate the quality of the present CMDS calculations. Therefore, for remote sensing applications, the temperature dependence of the velocity changing collisions frequency is the understudy of the group and will be presented in a forthcoming work.

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