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To cite this article: Wissam Fakhardji *et al* 2019 *J. Phys.: Conf. Ser.* **1289** 012021

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# Contribution from dimers to the collision-induced absorption spectra in an Ar–Kr gas mixture

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**Abstract.** We have developed an empirical Barker, Fisher and Watts (BFW) interatomic potential for the Ar–Kr pair along with a dipole moment computed from first principles using Møller–Plesset perturbation theory to second order (MP2). Using these results, we performed molecular dynamics calculations to compute the Ar–Kr collision induced absorption (CIA) spectrum at different temperatures. By comparing them to other calculations using a two body interaction treated with quantum mechanics, we have shown that the difference is due to the dimer’s contribution which grows in importance as the temperature is lowered.

## 1. Introduction

Quantum simulations are able to provide collision-induced absorption (CIA) spectra for two colliding particles but describing more than two-body interactions is not feasible in the frame of the quantum dynamical formalism. However, it has been shown that molecular dynamics (MD) is a useful tool to compute accurate collision-induced absorption spectra for different gaseous systems [1]. This technique allows for computation of CIA spectra at various temperatures and densities and therefore permits the exploration of purely two-body as well as three- or several-body interactions. In this study we investigated the contribution of the dimers to the absorption spectrum for the Ar-Kr system.

## 2. Theory

In a gas mixture, during the collision between two different atoms, a dipole moment  $\mu$  is induced, therefore the absorption of a photon becomes possible. In an isolated system of  $N$  classical particles the state at  $t_0 + t$  is uniquely determined by the conditions at the timestep  $t$ . The classical dipole autocorrelation  $\phi(t)$  is a function of the canonical variables and time. Therefore,  $\phi(t)$  is defined by the equation 1 [2]. By taking the real part of the Fourier transform of  $\phi(t)$ , one obtains  $C(\omega)$  (see equation 2). Finally the absorption coefficient is computed using equation 3.



$$\phi(t) = \sum_{i=1}^{N_p} \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} \frac{1}{4\pi\epsilon_0} \mu_i(t_0) \cdot \mu_i(t_0 + t) dt_0 \quad (1)$$

$$C(\omega) = \text{Re} \left\{ \frac{1}{\pi} \int_0^{\tau} \phi(t) e^{-i\omega t} dt \right\} \quad (2)$$

$$\alpha(\omega) = A \frac{4\pi^2}{3\hbar c} \exp\left(\frac{\hbar\omega}{2k_B T}\right) \omega \left[ 1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right) \right] \frac{1}{V} C(\omega) \quad (3)$$

with,  $A = \frac{(ea_0)^2}{4\pi\epsilon_0}$ ,  $e \approx 1.6 \times 10^{-19}$  C,  $a_0 \approx 5.3 \times 10^{-11}$  m,  $\epsilon_0 \approx 8.85 \times 10^{-12}$  C<sup>2</sup>/J.m,  $T$  = temperature,  $V$  = volume of the simulation box.

### 3. Numerical method

Firstly, the molecular dynamics part is performed using the open source software package LAMMPS. A simulation box, with periodic boundary conditions, containing a mixture of argon and krypton atoms, is defined. The atoms are randomly spread in the box and the initial speeds are given by the Maxwell-Boltzmann distribution at the temperature  $T$ . After this initialization step, the thermalization process begins at  $t_{therm}$  and continues until the system reaches equilibrium. The Berendsen thermostat (a LAMMPS option) is removed to let the system evolve freely. This timestep is taken from the time origin, and the system evolves over  $2\tau$  while the position of each particle at each atomic location is saved in an output file. Once the MD calculation is complete, the dipole autocorrelation, the Fourier transform and the absorption coefficient are computed using SpaCIAL (Spectra of Collision Induced Absorption with LAMMPS) an in-house Python code. Equation (1), the expression for  $\phi(t)$ , is implemented in the form of a sum as follows,

$$\phi(t) = \sum_{i=0}^{N_p} \frac{1}{M+1} \sum_{j=0}^M \frac{1}{4\pi\epsilon_0} \mu_i(j\Delta t) \cdot \mu_i(j\Delta t + t) \quad (4)$$

$N_p$  is the number of Ar–Kr pairs that satisfy the condition  $r < r_{cut}$ ,  $r$  being the interatomic distance while  $r_{cut}$  is the distance for which the dipole can reasonably considered as having a value of 0. The sum over  $M$  is the time averaging, the index  $j$  is shifted to become the new reference time until the maximum number defined by  $M = \frac{\tau}{\Delta t}$  is reached. The entire process (MD and post-processing with SpaCIAL) is repeated over many boxes with different initial conditions. Each independent simulation gives one CIA spectrum. The final result is an average of all the spectra collected over each box.

### 4. Pair potentials and dipole

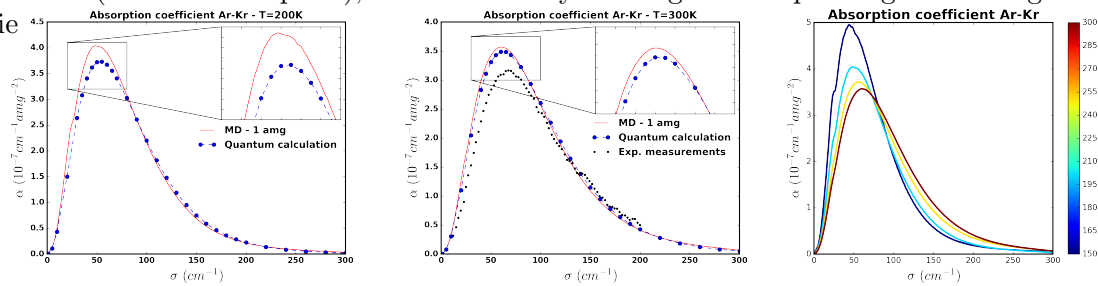
The interatomic potentials for each type of pair in the Ar–Kr system are needed to perform the MD simulations. The second step, i.e., the calculation of the dipole autocorrelation function  $\phi(t)$  requires the Ar–Kr dipole. The potential for the Ar–Ar and Kr–Kr pairs are taken from the work of Slaviček et al. [3] while we have developed one for the Ar–Kr pair as well as the dipole  $\mu(r)$ . The empirical Barker, Fisher and Watts (BFW) interatomic potential is determined from experimental values of viscosity, diffusion data, thermal conductivity and thermal diffusion factor. The dipole moment is computed from first principles using Møller–Plesset perturbation theory to second order (MP2) [5].

## 5. Results – Study of the dimer’s contribution and temperature dependence

In the QM approach, the system is treated as a two particle interaction and therefore gives only the free-free contribution to the spectrum. In the MD method, the model describes a many particle system where two and more body interactions occur. Hence in addition to free-free contributions, bound-free and bound-bound contributions are also contained included. Quantum mechanics and MD calculations have been run in order to study the dimer’s contribution on the CIA spectrum (see parameters in table 1).

$N_{atoms}^*$	$\rho^{**}$ (amg)	$t_{therm}$ (ps)	$\tau$ (ps)	$\Delta t$ (fs)	$r_{cut-off}(a_0)$
$2.5 \times 10^6$	1.0	100.0	10.0	50.0	20.0

**Table 1.** Settings for the MD calculations – \* Equivalent to 50 simulation boxes of  $5.0 \times 10^4$  atoms each (50% of each specie), \*\* Total density of the gas corresponding to 0.5 amg for each specie



**Figure 1.** Left and center figures: Comparison between MD, quantum mechanics calculations and experimental measurements [4] of CIA spectrum at T=200K and T=300K – Right figure: temperature dependence of the absorption coefficient

The difference between the MD and the QM spectra is due to the dimer’s contribution which becomes more important as the temperature is lowered. At T=300K, the MD and quantum results are also compared to some experimental measurements performed at 200 amg [4]. Although the pressures are different, this comparison is useful in order to check the shape and the order of magnitude at T=300K. Several CIA spectra have been computed for different temperatures using MD with the settings in table 1. On figure 1 one can observe that, at low temperature, the spectrum shows some structures while it is smooth at higher temperature. These structures are signatures of bound-free and bound-bound transitions which increase with decreasing temperature. This has been verified with quantum calculations where the three contributions (free-free, bound-free and bound-bound) have been computed separately, their sum yielding a spectrum very close to the one produced by the MD method [5].

## 6. Conclusion

Having developed a dipole and a potential for the Ar–Kr pair, we have computed CIA spectra with the MD method and, for comparison, the QM approach. The difference between the MD and QM spectra, which is due to the dimers contribution, has been observed by comparing the results at T=200K and T=300K. A study of the temperature effects has shown that the role of the dimers in the CIA spectrum becomes more important as the temperature is lowered as expected and verified with quantum calculations [5].

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