Influence of the nanodroplet size, interaction potential and vibrational energy gap on the vibrational relaxation of diatomic molecules in superfluid helium nanodroplets

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1. INTRODUCTION

The study of reactions and energy transfer processes involving ^{4}He superfluid nanodroplets [HeNDs (quantum fluid); T=0.37 K] and atoms or molecules is gaining progressively more interest in Chemistry.[1,2] The vibrational energy relaxation (VER) of a homonuclear diatomic molecule in a ^{4}He superfluid nanodroplet (HeND) was studied using a hybrid quantum approach proposed by us.[3,4,5,6] This work extends a previous contribution of our own on the VER of the I_2(X) molecule in HeNDs,[5] and corresponds to the second theoretical investigation reported so far on this interesting problem.
The VER from v=1 to v=0 of I_2(X) embedded in a 100 ^{4}He atoms nanodroplet has been taken as reference system and a number of situations has been simulated: (1) number of ^{4}He atoms (50-200); (2) "He-I_2" interaction potential energy from 0.5 to 1.5 times the real He-I_2 interaction; (3) "I_2" (or X_2) v:0-1 vibrational energy gap from 0.75 to 1.5 times the real I_2 energy gap.

2. THEORETICAL METHOD

Hybrid approach

- ^{4}He : Phenomenological TDDFT (*Time Dependent Density Functional Theory)* using the Orsay-Trento functional[7]

- X_2 : Standard time dependent quantum mechanics (wave function)

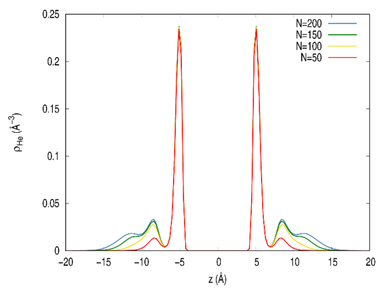
$$i\hbar\frac{\partial}{\partial t}\Psi_{He}(\boldsymbol{R}_{He}) = \left[-\frac{\hbar^2}{2m_{He}}\boldsymbol{\nabla}^2 + \int dr\, V_{He-X_2}(r,\boldsymbol{R}_{He})\left|\varphi_{X_2}(r)\right|^2 + \frac{\delta\mathcal{E}_c[\rho_{He}]}{\delta\rho_{He}}\right]\Psi_{He}(\boldsymbol{R}_{He})$$

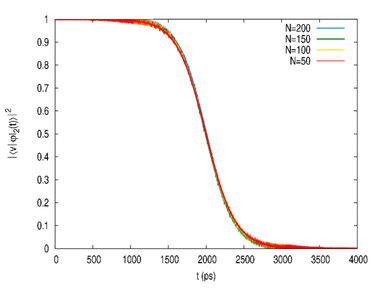
$$i\hbar\frac{\partial}{\partial t}\varphi_{X_2}(r) = \left[-\frac{\hbar^2}{m_{X_2}}\frac{\partial^2}{\partial^2 r} + \int d\boldsymbol{R}_{He} V_{He-Cl_2}(r,\boldsymbol{R}_{He})\rho_{He}(\boldsymbol{R}_{He})\right]\varphi_{X_2}(r)$$

To make this study possible, we have expressed the X_2 wave function in terms of the vibrational basis functions of the free X_2 molecule (which is described by a Morse potential energy function). See refs 5 and 6.

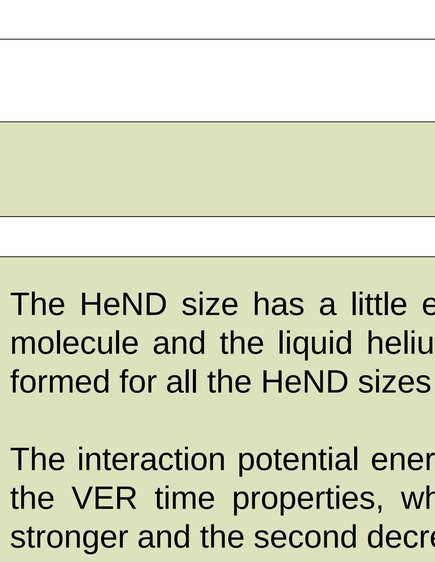
3. RESULTS AND DISCUSSION

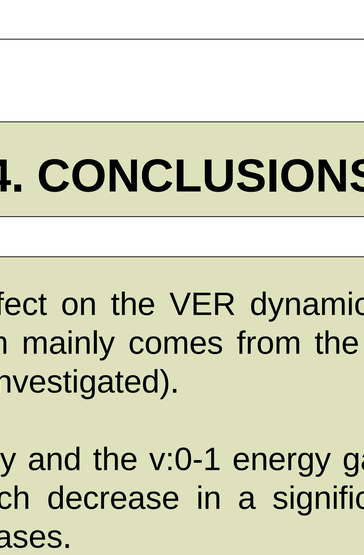
3.1. Vib. relaxation and nanodroplet size $I_2@^4He_N$

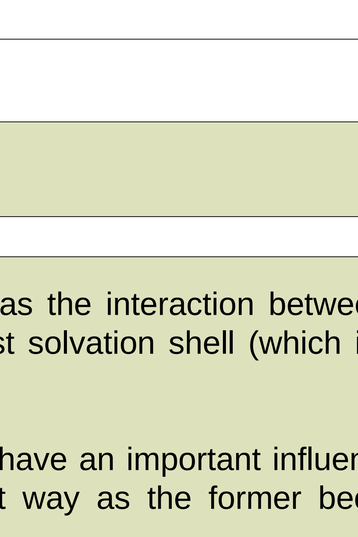




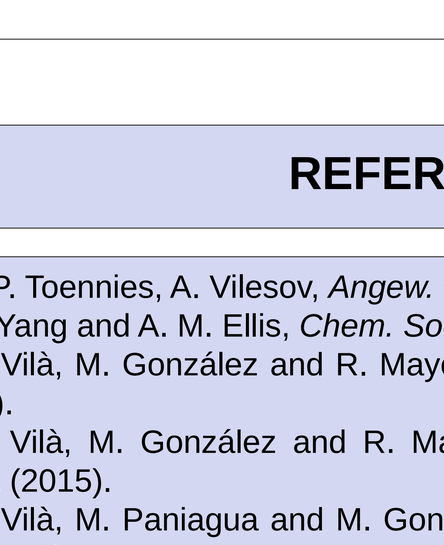
3.2.Vib. relaxation and interaction potential energy $X_2@^4He_{100}$

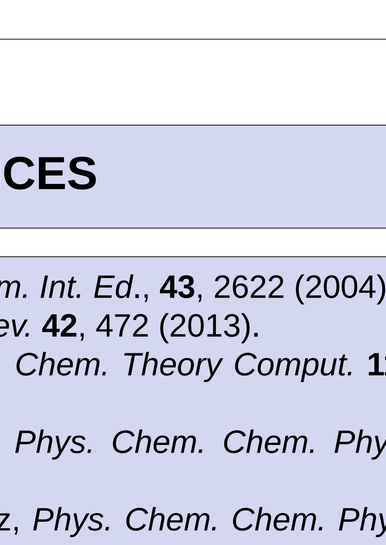






3.3. Vib. relaxation and vibrational energy gap $X_2@^4He_{100}$





4. CONCLUSIONS

- The HeND size has a little effect on the VER dynamics, as the interaction between the molecule and the liquid helium mainly comes from the first solvation shell (which is fully formed for all the HeND sizes investigated).
- The interaction potential energy and the v:0-1 energy gap have an important influence on the VER time properties, which decrease in a significant way as the former becomes stronger and the second decreases.
- The molecule-helium interaction energy is hardly modified during the relaxation process, but it shows oscillations during the transition. Thus, the HeND structure is essentially unchanged.
- An interpretation based on the coupling terms, $\langle V_{01}^2\rangle$, between the two vibrational levels involved and the oscillator velocity (that is proportional to $\nu_e^{1/2}$) has been attempted.

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