

The construction of a reliable potential for GeO_2 from first-principles

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The construction of a reliable potential for GeO_2 , from first-principles, is described. The obtained potential, which includes dipole polarization effects, is able to reproduce all the studied properties (structural, dynamical and vibrational) to a high degree of precision with a single set of parameters. In particular, the infrared spectrum was obtained with the expression proposed for the dielectric function of polarizable ionic solutions by Weis *et al.* [J.M. Caillol, D. Levesque and J.J. Weis, *J. Chem. Phys.*, **91**, 5544 (1989)]. The agreement with the experimental spectrum is very good, with three main bands that are associated to tetrahedral modes of the GeO_2 network. Finally, we give a comparison with a simpler pair-additive potential.

I. INTRODUCTION

In the vitreous and liquid states, at ambient pressure, germania (GeO_2) (a close structural analog of silica (SiO_2)) forms a tetrahedrally coordinated three-dimensional network¹. Because of its lower abundance, its usage in practical applications is much less widespread than for the SiO_2 . Still, GeO_2 is used in several fields, mainly related to optical technologies. For example, a mixture of SiO_2 and GeO_2 allows precise control of refractive index in optical fibres and waveguides. It is of interest to develop simulation methods to allow a detailed examination of the local structure in such mixtures and to predict the infrared spectrum, since this determines the long wavelength limit for their use as optical fibres.

The essential similarity between the structures of glassy GeO_2 , SiO_2 and BeF_2 was made clear by the study of vibrational properties by Galeener and co-workers² who showed that the inelastic neutron, infrared and Raman spectra of the different materials were closely related. More recent infrared studies of GeO_2 have also been reported^{3,4}. Recently a full set of partial structure factors were determined in this system by using the method of isotopic substitution in neutron diffraction experiments^{5,6}. The results show that the tetrahedral network structure is based on corner sharing $\text{Ge}(\text{O}_{1/2})_4$ tetrahedra with a Ge-O average distance of 1.73 Å and with a mean inter-tetrahedral Ge-O-Ge angle of 132°. They also show that the topological and chemical ordering in the network display two characteristic length scales at distances greater than the nearest neighbour.

Several molecular dynamics (MD) simulations have been undertaken to study the structural and vibrational properties of the disordered phases of GeO_2 . Classical MD simulations were performed on glassy and liquid GeO_2 ^{7,8}, using pairwise additive potentials with partial charges developed by Oeffner and Elliott (OE) for modeling the α -quartz and rutilelike phases of GeO_2 ⁹. More recently, first-principles molecular dynamics (FPMD) of glassy GeO_2 have also been reported^{10,11}. In principle, the amount of empirical information needed to set up a

first-principles calculation is minimal and it would normally be the method of choice to study the physico-chemical properties of condensed phase systems. However, it is computationally very expensive compared to classical molecular dynamics, which is a major drawback when dealing with glassy systems. Classical and FPMD simulations were also compared one with each other in a combined study¹² for temperatures above 2530 K. In this study *apparent* inconsistencies between the properties predicted by the classical simulations of different authors are noted. In reality, two *different* parameter sets were proposed by OE: an original one, which was fitted from an *ab initio* energy surface, and a so-called rescaled one, which was developed from the previous one in order to give a better reproduction of the vibrational properties. For example, the partial charge of the germanium ion was shifted from 1.5 e in the original potential to 0.94174 e in the rescaled potential. The apparent inconsistencies arise because different classical potentials were being used. Our objective is a single potential which will give a good description of structure and dynamics and allow long simulations on systems of many atoms.

The structure of the simulated system can directly be compared with the neutron / X-ray diffraction experiments. Both classical and FPMD simulation provide structure factors which are in rather good agreement with experiments. For the classical molecular dynamics, the most noticeable difference is a shift to high q -values of the first sharp diffraction peak (FSDP), which was observed with both versions of the OE potential^{7,8}. As this peak is associated to medium range distances⁵, this means that the Ge-O-Ge bond angle is too large and the topology of the tetrahedral network is not correctly described. The FPMD simulations provide a diffraction pattern with improved agreement¹¹, but the small size / timescales explored lead to large statistical uncertainties, mainly in the region of this FSDP. The vibrational properties can also be straightforwardly calculated. The vibrational density of states (VDOS) was estimated from FPMD and classical MD using the rescaled OE potential, with an overall reasonable agreement with the available experimental data extracted from inelastic neutron scat-