COMPUTER ANALYSIS OF SOLID, LIQUID AND GAS PHASE PROPERTIES OF SULPHUR DIOXIDE

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Abstract

Intermolecular effective pair potential for sulphur dioxide obtained by the molecular dynamics simulation of liquid was previously applied to the gas phase and now is also used to calculate the solid state properties. It is concluded that this type of the potential is not adequate for description of the crystal structure and dynamics.

INTRODUCTION

One of the principal aims of theoretical studies in the field of molecular physics is the investigation of the intermolecular potentials. There are two main approaches to the solution of this problem. The first one is to use the ab initio methods of quantum chemistry which despite the enormous calculational efforts give the results which are often below the expectations except for some particular cases (N_2 for instance [1]). The other approach is to assume some analytical form of the intermolecular potential and to fit the free parameters. The milestone of this approach is the classical work of Hirschfelder et al. [2]. There, the potentials of the one-site type were fitted to viscosity and second virial coefficient data. Another source of potential data are the crystal dynamics calculations. In the case of sulphur dioxide there are two such calculations [3, 4]. The particular impetus to the field was given by the development of the computer simulation methods. Much more sophisticated potentials could be considered in that case. Our objective in this work is to concentrate on solid state properties of SO_2, and to see how well are they reproduced by potentials from different sources. A general comparison of all existing potentials is already given in [5]. A particular emphasis is on potentials obtained by us [6] on the liquid state by molecular dynamics simulation method. By this test the transferability of the potential from one state of matter to the other is also checked.

RESULTS

We are going to give a very brief presentation of liquid and gas properties of sulphur dioxide, to discuss much more thoroughly the solid state properties. We have done molecular dynamics simulation of the liquid sulphur dioxide with four different intermolecular effective pair potentials. In this way one can follow how the introduction of additional complexities in the potential influences the physical properties of the model. Because of the fact that this analysis is presented in several already published papers [6 – 8] we shall restrict ourselves to some general statements.

In the molecular dynamics study we have chosen the energy and pressure at four points on the liquid-vapour coexistence curve as the properties to be fitted, and the free parameters of the potential were determined. It is clearly seen that the reliability of the potential depends upon the physical property we are looking at. Self-diffusion coefficient is one of the properties which is well reproduced by all potentials, and specific heat capacity is on the other hand not well reproduced even with the most sophisticated potential.

The second virial coefficient of the SO_2 vapour is well reproduced by our potentials and one can follow the improvement when going to more detailed potentials [9].

Table I: Atom-atom potentials

Potential	A (J nm^6 mol^{-1})	$Bx10^{-8}$ (J mol^{-1}) $B'x10^3$ (J nm^{12} mol^{-1})	$Cx10^{10}$ (m)
Kuroda and Machida [3] $V = -\frac{A}{r^6} + B\exp(-Cr)$	S-S 5.986	9.243	3.62
	S-O 2.240	8.492	4.085
	O-O 0.837	7.803	4.55
Rastogi et al. [4] $V = -\frac{A}{r^6} + \frac{B'}{r^{12}}$	S-S 7.979	111.8	
	S-O 5.291	2.679	
	O-O 4.529	3.089	
Sokolić et al. [6] $V = -\frac{A}{r^6} + \frac{B'}{r^{12}}$	S-S 13.044	27.46	
	S-O 4.856	6.070	
	O-O 1.720	1.206	

It is interesting to see how successfully we can apply these potentials (see Table I) to the solid SO_2. The crystal structure of SO_2 is presented in Fig. 1. The space group of the lattice is Aba2 (C^{17}_{2v}). Experimental lattice parameters are given in Table II. The molecules indicated in bold lines in Fig. 1 from the primitive lattice cell. In the first column of the Table II the experimental frequencies of external vibrational modes and the lattice energy are listed. θ is the angle between the plane of the molecule and the ac crystallographic plane.

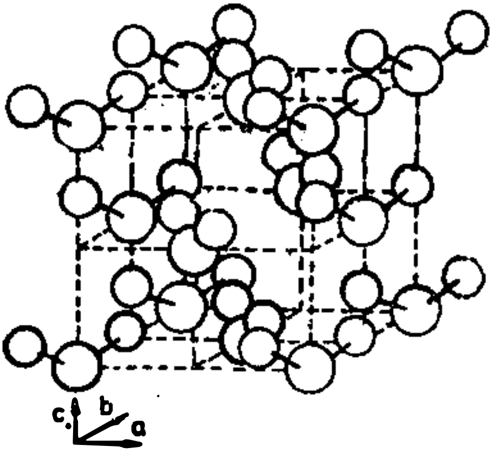

Fig. 1. Arrangement of molecules in the unit cell

In the column A of Table II the original calculations of Kuroda and Machida are presented with three-site Buckingham potential (potential I in ref. [3]), see Table I. In their calculations they used the Shymanouchy method which neglects the first derivatives of the atom-atom potential. This is incorrect when being out of equilibrium crystal

Table II – Lattice frequencies and energy of crystalline SO_2

Observed frequencies [11] (cm^{-1})	Kuroda and Machida			Rastogi et al. [4]		Sokolić et al. [6]	
	A[3]	B	C	D	E	F	G
164	106	105	94	153	136	180	104
141	100	100	86	134	108	174	96
103	64	60	68	86	91	97	94
94	60	54	65	86	79	83	76
85	56	52	60	81	65	78	59
81	45	34	54	69	63	57	49
76	42	30	37	52	62	41	49
71	37	27	33	44	52	38	44
68	22	20i	15	40	43	40i	24
Lattice energy (kJ mole^{-1}) −38.47	−14.40	−19.72	−40.86	−40.86	−41.61	−29.34	
Lattice parameters (in 10^{-10} m)							
a = 6.07	5.15			6.12		6.81	
b = 5.94	7.95			6.15		5.93	
c = 6.14	5.32			5.95		5.98	
$\theta = 46.3°$	90°			48.1°		31.9°	

structure. We repeated the calculation with the same potential taking into account the first derivatives and the result is given in column B. It is seen that one imaginary frequency appears, which menas that the crystal with this potential is unstable with respect to this deformation. In the following calculation the minimization of total crystal energy is performed. The respective crystal lattice parameters are given in column C of Table II together with vibrational frequencies.

Next, the Rastogi et al. three-site Lennard-Jones potential [4] (see Table I) was analyzed. In column D the vibrational frequencies and lattice energy are given for experimental crystal lattice. They have also minimized the lattice energy and obtained the results given in column E.

Results with our three-site Lennard-Jones potential obtained from the simulation of the liquid (see Table I) are given in column F for observed and in G for minimized crystal lattice.

In Table II we represent vibrational frequencies only for wave vector k = 0. Within the Brillouin zone we systematically obtain several imaginary frequencies.

DISCUSSION

There are several possible reasons for our inability to describe dynamical properties of solid SO_2 (i.e. phonon dispersion curves) within our simple model. The first possible reason is that the atom-atom potentials obtained by fitting the liquid properties are not enough orientationally sensitive, because for most of the properties in this phase the orientational dependence is relatively weak. The other explanation for unstable lattice obtained in our calculations is that our potential function is too crude. It means that simple atom-atom potentials (of Buckingham or Lennard-Jones type) do not describe satisfactorily the intermolecular interaction without taking into account the electrostatic multipoles. The polarisability of the molecule could play an important role in the case of SO_2 and our model, treating molecule as unpolarisable, was incomplete. One of possible alternative calculations within the frame of shell model could probably give better description of statical and dynamical properties of solid SO_2. The other alternative is a better description of molecular multipoles using atom or bond multipoles [10].

We hope that the future calculations will give us the more complete insight into the intermolecular interaction in the crystaline SO_2.

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