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**PAIR POTENTIALS FOR ALUMINA FROM *AB INITIO* RESULTS
ON THE Al_2O_3 MOLECULE**

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Abstract

We use results from an *ab initio* investigation by Chang *et al.* on energetically low-lying stationary points of the Al_2O_3 molecule to determine interionic potentials for the Al-O, O-O and Al-Al pairs. Our results are discussed in the perspective of previous studies of the condensed phases of alumina, with special regard to the structure of its molten state.

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1. INTRODUCTION

The alumina mineral Al_2O_3 is a ceramic material with a great deal of technical and industrial applications in both its solid and liquid states. Crystalline polymorphs of alumina, and especially the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase, have been studied very extensively [1]. Whereas in $\alpha\text{-Al}_2\text{O}_3$ the Al ion is sixfold coordinated by oxygens, both fourfold and sixfold coordination states are present in different proportions in the metastable $\gamma\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ crystal phases. The liquid pair structure of Al_2O_3 as determined by X-ray diffraction on levitated samples in containerless confinement [2] indicates that a main fraction of the Al ions are fourfold coordinated, the average first-neighbour coordination number being 4.4 ± 1.0 . These results imply that alumina undergoes a major structural rearrangement on melting.

In a previous contribution to this Journal two of us [3] used a simple rigid-ion model to evaluate the local sixfold- and fourfold-coordinated structures for the Al ion by the device of attributing fractional charges to the surrounding oxygens in order to allow for oxygen sharing. We found that the Al-O bond length drops from 1.91 Å to 1.71 Å with the drop in coordination, the latter value being in excellent agreement with the position of the main peak in the X-ray pair distribution function $g_X(r)$ at 1.76 Å. There also was approximate agreement between the calculated average O-O bond length at 2.78 Å and the position of the second peak in $g_X(r)$ at 3.08 Å. Finally, we suggested that the connectivity of the alumina melt should arise from oxygen sharing between tetrahedral units and evaluated the specific case of edge sharing.

A molecular dynamics study of a rigid-ion model for liquid alumina by Gutiérrez *et al.* [4] has confirmed this elementary picture and enriched it with a lot of fascinating detail. The liquid structure that they find mainly consists of somewhat distorted tetrahedral AlO_4 basic units which are linked through corner, edges and faces, this conclusion being drawn from detailed analyses of the distributions of bond angles and of ring statistics. The main Al-O and O-O bond lengths at 1.75 Å and 2.75 Å are in excellent agreement with our earlier estimates, while the nearest-neighbour Al-

Al bond length lies at 3.15 Å. A further significant quantitative result is that the distribution of Al-O-Al bond angles peaks at 95°, against the value 109.47° for the ideal tetrahedron.

In the present work we explore other coordination states for the Al ion by oxygens in a different aggregation state of Al₂O₃, *i.e.* the isolated monomeric molecule. The source of data for our study is the *ab initio* evaluation of stationary points in the potential energy landscape for this molecule carried out by Chang *et al.* [5] at the Hartree-Fock plus second-order Møller-Plesset frozen-core level of approximation. We focus in particular on the stationary points represented by (i) the D_{∞h} linear molecule, which in the calculations of Chang *et al.* lies at only 0.1 eV above their C_{2v} kite-shaped spin-triplet ground state; and (ii) the D_{3h} trigonal bipyramid, which lies rather high in energy (2.09 eV above the D_{∞h} state). These two molecular states have total spin S = 0 and show twofold and threefold coordination of the Al ion, respectively.

A main purpose of our study is to examine the usefulness of a simple rigid-ion model in describing molecular units in which the binding has traditionally been viewed as arising from covalency. As a background we recall that model calculations on crystalline oxides have usually involved rather complex treatments of the ionic polarizabilities [6 -9] and the inclusion of three-body forces [10], whereas useful information has been gained by much simpler rigid-ion models on γ-Al₂O₃ [11, 12] and on liquid Al₂O₃ [3, 4]. Of course, a simple ionic model cannot deal with asymmetric molecular shapes nor with spin multiplets: hence our choice of the above two stationary points for the Al₂O₃ molecule out of all those found in the calculations of Chang *et al.* [5].

2. EVALUATION OF STATIC AND DYNAMIC MOLECULAR STRUCTURES

The ionic model that we examine assumes pairwise-additive interaction potentials $V_{ij}(r)$ between ions of species i and j . These are the sum of Coulomb interactions described by effective ionic valences z_i (subject to overall charge neutrality) and of short-range overlap energies having the form proposed by Busing [13]. Namely,

$$V_{ij}(r) = \frac{z_i z_j e^2}{r} + f(\rho_i + \rho_j) \exp\left(\frac{R_i + R_j - r}{\rho_i + \rho_j}\right) \quad (1)$$

The overlap repulsive term in Eq. (1) involves as disposable parameters the ionic radii R_i and the stiffness constants ρ_i . We recall that only the relative magnitude of R_{Al} and R_O is physically significant as a measure of the relative size of the two ions, since their absolute magnitudes depend on the energy scale as set by the pre-exponential factor f [14].

As a first step towards the determination of the model parameters we focus on the linear $O^T-Al-O^B-Al-O^T$ molecule, with the symbols T and B denoting terminal and bonding oxygens. In this configuration only the Al-O overlap repulsions are relevant in determining the Al- O^T and Al- O^B bond lengths, which from the calculations of Chang *et al.* [5] are 1.629 Å and 1.692 Å, respectively. These authors also discuss the experimental evidence on vibrational spectra of Al_2O_3 molecules and assign the observed infrared-active vibration at $1170 \pm 50 \text{ cm}^{-1}$ to the σ_u^+ normal mode having the highest frequency in the linear molecule. By fitting these three data we obtain as first estimates corresponding to the choice $f = 0.05 \text{ e}^2/\text{Å}^2$ [13] the results $R_{Al} + R_O = 1.82 \text{ Å}$, $\rho_{Al} + \rho_O = 0.10 \text{ Å}$ and $z_{Al} = 1.2$. The value that we obtain for the effective valence is crucially dependent on the energy scale of the vibrational modes and can be interpreted as showing that electron transfer from Al to oxygen in the molecule is only partial. For comparison we recall that the values $z_{Al} = 1.65$ and $z_{Al} = 1.45$ have been adopted in previous models for γ - Al_2O_3 [12] and for liquid alumina [4], respectively. Such values are therefore roughly consistent with the evidence on the linear Al_2O_3 molecule.

We turn next to the D_{3h} trigonal bipyramid, in which a regular triangle of oxygens binds the two Al ions at the opposite apices. It is quite pleasing to find that the above modelling of the linear Al_2O_3 molecule already yields not unreasonable values for the static structural parameters of the Al_2O_3 bipyramid. Specifically, without further adjustment of model parameters we find for the latter an Al- O^B bond length of 1.71 Å against the *ab initio* value of 1.827 Å and an O-Al-O bond angle of 82° against the *ab initio* value of 91.2° . These discrepancies are remedied by allowing for the O-O overlap repulsions in the bipyramid, as we do by fitting the *ab initio* value of the O-Al-O bond angle under the assumption that only the Coulomb repulsions are operative between the Al ions.

The final values of our model parameters are reported in the first row of Table I. Comparisons of our results with the *ab initio* values of the structural parameters and of the vibrational frequencies of the two Al₂O₃ molecular isomers are shown in Table II and Table III, respectively. As suggested by Chang *et al.* [5], their calculated vibrational frequencies have been reduced by a factor of about 0.94 in order to force agreement with the observed σ_u^+ mode of the linear isomer at $1170 \pm 50 \text{ cm}^{-1}$.

It is clear from Table II that quite a good description has been obtained for the static structure of these molecules by the simplest of models with a minimal number of fitting parameters. The residual minor discrepancies probably are within the likely uncertainties of the *ab initio* calculations. It is seen from Table III, on the other hand, that the vibrational frequencies are more sensitive to the details of the model. The agreement with the *ab initio* values of the mode frequencies is in fact very pleasing for the linear Al₂O₃ isomer, especially for the stretching-type modes in the upper part of the spectral range. Refinements of the model seem instead necessary to obtain a more reasonable account of the vibrational modes in the bipyramidal isomer.

3. COMPARISON WITH LIQUID Al₂O₃ AND CONCLUDING REMARKS

The second row in Table I reports the values of the parameters for the interionic pair potentials used by Gutiérrez *et al.* [4] in their study of liquid Al₂O₃ by molecular dynamics. Although the individual values of the parameters that we have obtained from the *ab initio* results on molecular Al₂O₃ are quite different from theirs, the actual interionic potentials for both the Al-O and O-O pairs are qualitatively very similar. This is seen from Figure 1, which plots our results for $V_{\text{Al-O}}(r)$ and $V_{\text{O-O}}(r)$ in comparison with theirs. We do not show the potentials in the distance range below $r = 1 \text{ \AA}$, where an unphysical divergence arises in $V_{\text{Al-O}}(r)$ especially if van der Waals interactions are included.

As can be seen from Figure 1, the main qualitative differences between the two sets of interaction models are an upward shift and a short-range stiffening in the molecular-type potentials. The former feature is clearly due to the lowering of the effective valences in the

molecular states (see Table I) and its main consequence would be a lowering of the calculated cohesive energy of the condensed phase. A stiffening of the short-range repulsions may instead be expected to sharpen the calculated shape of the first-neighbour shell in the liquid and to increase the average O-O distance, thus leading to better agreement with the X-ray pair distribution function measured by Ansell *et al.* [2].

Thus, in conclusion, we have shown that there is broad consistency between pair-potential interaction models for the structure of molecular and condensed phases of Al_2O_3 . More generally, the structure of ionic materials is primarily determined by Coulomb interactions and by ionic radii, so that it can be evaluated at an almost fully quantitative level by means of models incorporating a wise choice of these system parameters. Of course, such models will miss the more subtle distortions in the atomic and electronic structure that may be present in a static picture of both the crystal phases and the molecular isomers: however, such distortions will to a good extent be averaged out by thermal fluctuations in high-temperature materials such as liquid or gaseous Al_2O_3 . On the contrary, predictions of dynamical structure and of thermodynamic properties may require considerable sophistication in the model interactions.

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TABLE I. Ionic-model parameters for the Al_2O_3 molecules and for liquid Al_2O_3 .

	f ($\text{e}^2/\text{\AA}^2$)	z_{Al}	z_{O}	R_{Al} (\AA)	R_{O} (\AA)	ρ_{Al} (\AA)	ρ_{O} (\AA)
Molecules	0.05	1.2	- 0.8	0.50	1.34	0.0	0.10
Liquid ^a	0.003	1.4175	- 0.9450	0.7852	1.8215	0.034	0.138

^a From Gutiérrez *et al.* [4]. These authors also include van der Waals attractions in their model.

TABLE II. Bond lengths and bond angles in the $\text{D}_{\infty\text{h}}$ (linear) and $\text{D}_{3\text{h}}$ (bipyramidal) Al_2O_3 molecules.

	$r_{\text{Al-O}^{\text{B}}}$ (\AA)	$r_{\text{Al-O}^{\text{T}}}$ (\AA)	$R_{\text{Al-Al}}$ (\AA)	$R_{\text{O-O}}$ (\AA)	$\angle\text{O-Al-O}$
$\text{D}_{\infty\text{h}}$: present ^a	<u>1.692</u>	1.65	3.38	3.34	180°
<i>ab initio</i> ^b	1.692	1.629	3.384	3.321	180°
$\text{D}_{3\text{h}}$: present ^a	1.77	--	2.01	2.53	<u>91.2°</u>
<i>ab initio</i> ^b	1.827	--	2.065	2.611	91.2°

^a Underlined values have been fitted to the *ab initio* results.

^b From Chang *et al.* [5].

TABLE III. Vibrational frequencies for the $\text{D}_{\infty\text{h}}$ (linear) and $\text{D}_{3\text{h}}$ (bipyramidal) Al_2O_3 molecules (in cm^{-1} ; numbers in parentheses give the mode multiplicity).

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
$\text{D}_{\infty\text{h}}$: present ^a	42 (2)	80 (2)	209 (2)	391	889	1085	<u>1171</u>
<i>ab initio</i> ^b	33 (2)	165 (2)	238 (2)	404	873	1068	1170
$\text{D}_{3\text{h}}$: present ^a	382 (2)	422 (2)	445	501	637 (2)	819	--
<i>ab initio</i> ^b	318 (2)	397 (2)	543	622 (2)	648	751	--

^a The underlined value has been fitted to experiment.

^b From Chang *et al.* [5].

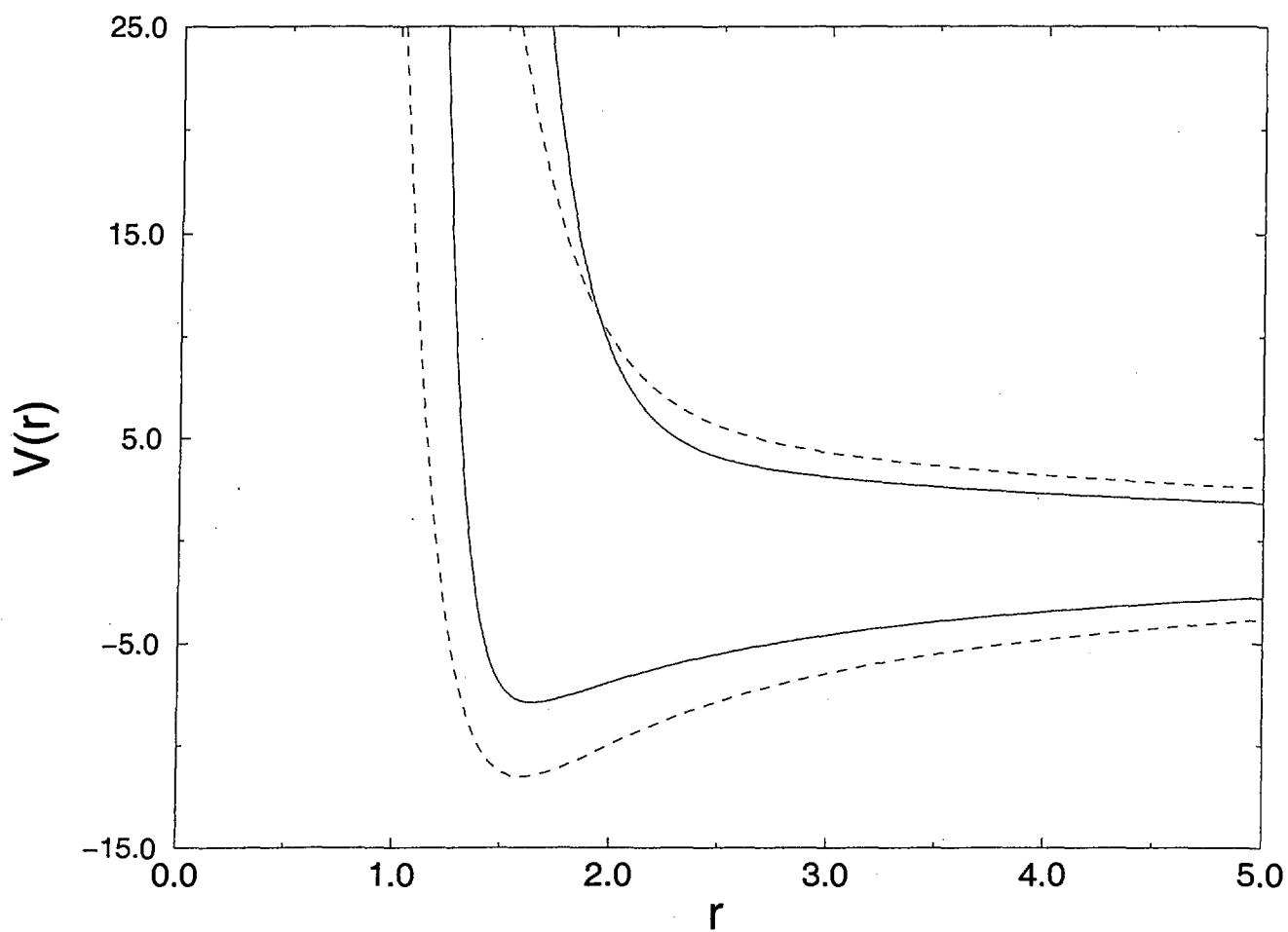


Figure 1. Interionic potentials $V(r)$ (in eV) versus interionic distance r (in Å) from molecular Al_2O_3 (full curves), compared with model interactions for liquid Al_2O_3 (dashed curved). The lower curves show $V_{Al-O}(r)$ and the upper ones $V_{O-O}(r)$.