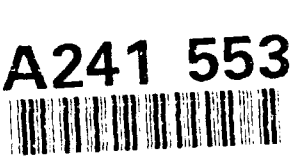

TECHNICAL REPORT BRL-TR-3268

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MONTE CARLO CALCULATIONS OF THE PROPERTIES OF SOLID NITROMETHANE

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SEPTEMBER 1991

U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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13. ABSTRACT (Maximum 200 words)

Pairwise additive potential energy functions for H-O, H-H, and O-O intermolecular interactions are presented; methods by which these functions were developed are discussed, and preliminary Monte Carlo calculations of the crystal lattice parameters using these functions are presented. The results indicate that these potential energy functions correctly reproduce the lattice parameters measured by neutron diffraction at 4.2 K, ambient pressure, and at pressures below 1.0 GPa, room temperature.

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1. INTRODUCTION

It is our intention in this and future work to obtain sufficient information concerning the intermolecular interactions between molecules of nitromethane (CH_3NO_2) in order to produce, via computer simulation, a reliable equation of state and other related properties in the condensed phase. For this purpose, substantial experimental investigations have been performed in the past on several properties of the crystal. For the present study, the most important of these are the determination of the crystal structure at ambient pressure, from 4.2 K to 228 K (Trevino, Prince, and Hubbard 1980) and neutron spectroscopic determination of the rotational properties of the methyl group (Trevino and Rymes 1980; Alefeld et al. 1982; Cavagnat et al. 1985). The crystal structure has also been determined at room temperature to a pressure of 6.0 GPa (Cromer, Ryan, and Schiferl 1985). The neutron spectroscopy was instrumental in allowing an accurate mathematical description of the rotational potential of the methyl group. Additionally, the activation energy for rotational diffusion was obtained with quasi-elastic neutron scattering. All of these properties are principally functions of the intermolecular interactions. In particular, the rotational barrier must be due to the intermolecular interactions since the gas phase internal barrier to rotation is vanishingly small (0.006 kcal/mol) (Tannenbaum et al. 1954; Tannenbaum, Myers, and Gwinn 1956). Since it is our intention to produce a reliable equation of state by simulation techniques, it is imperative to use functions which accurately describe the potential energy of the crystal. The validity of such potentials can only be determined by insisting that they reproduce as much experimental data as can be obtained. We will describe the methods by which potentials between H-O, H-H, and O-O atoms have been obtained in light of the previous experimental measurements and several consequences of these potentials which infer their reliability.

2. DISCUSSION OF EXPERIMENTAL EVIDENCE

CH_3NO_2 at ambient pressure freezes at 244 K, and at room temperature at a pressure of approximately 0.3 GPa. The crystal structure at ambient pressure has been determined by single crystal x-ray diffraction of the protonated crystal and neutron powder diffraction of the fully deuterated crystal (Trevino, Prince, and Hubbard 1980). The single crystal x-ray diffraction was performed at 220 K, and the neutron diffraction was performed at 4.2–120 K. The crystal structure was found to be the same at all temperatures and pressures mentioned

previously. The orientation of the methyl group, however, is substantially altered as a function of pressure. It is found that at ambient temperature below a pressure of 3.5 GPa, the rotation of the methyl group is only slightly hindered (Cromer, Ryan, and Schiferl 1985). At 3.5 GPa, the x-ray diffraction data inferred that the rotation of the methyl group was substantially hindered and that it was rotated 45° from that found by neutron diffraction at 4.2 K, ambient pressure. The neutron diffraction study as a function of temperature is consistent with a low barrier to rotation of the methyl group about the C-N bond (Trevino, Prince, and Hubbard 1980). Indeed, the quasi-elastic neutron scattering which measured the residence time between the thermally activated rotational jumps as a function of temperature suggested an activation energy of 10 meV for this motion (Trevino and Rymes 1980). These diffraction studies are also consistent with a rotational potential of three-fold symmetry. The study also revealed that all methyl groups experience the same environment. The tunnel splitting of the ground state and the position of the first and second excited rotational states in both isotopic species have been measured by inelastic neutron scattering (Cavagnat et al. 1985). These values were studied as a function of pressure to 0.5 GPa, all at 4.2 K. From this plethora of data, a reliable description of the potential energy experienced by the methyl group as it rotates in the crystal was obtained.

In Figure 1 is displayed the potential energy as a function of methyl group rotation which accurately reproduces the measured torsional energy levels and has three-fold symmetry as required by the previous experimental measurements. The structure of this curve was found to be absolutely necessary to reproduce the spectroscopy. These studies provide a most comprehensive set of criteria which intermolecular interactions must satisfy.

3. INTERMOLECULAR INTERACTIONS

Two calculations of the rotational potential using pairwise additive interatomic interactions between neighboring molecules in the crystal have been performed previously (Cavagnat et al. 1985; Cavagnat and Pesquer 1986). Both studies agree that insofar as the description of $V(\theta)$ shown in Figure 1, the interaction of principal importance is that between H atoms on the methyl group and O atoms of the NO_2 group of neighboring molecules. Although both studies reproduce the shape of $V(\theta)$ using typical pairwise additive potential functions, neither was successful in obtaining the measured orientation of the methyl group in the crystal at 4.2 K.

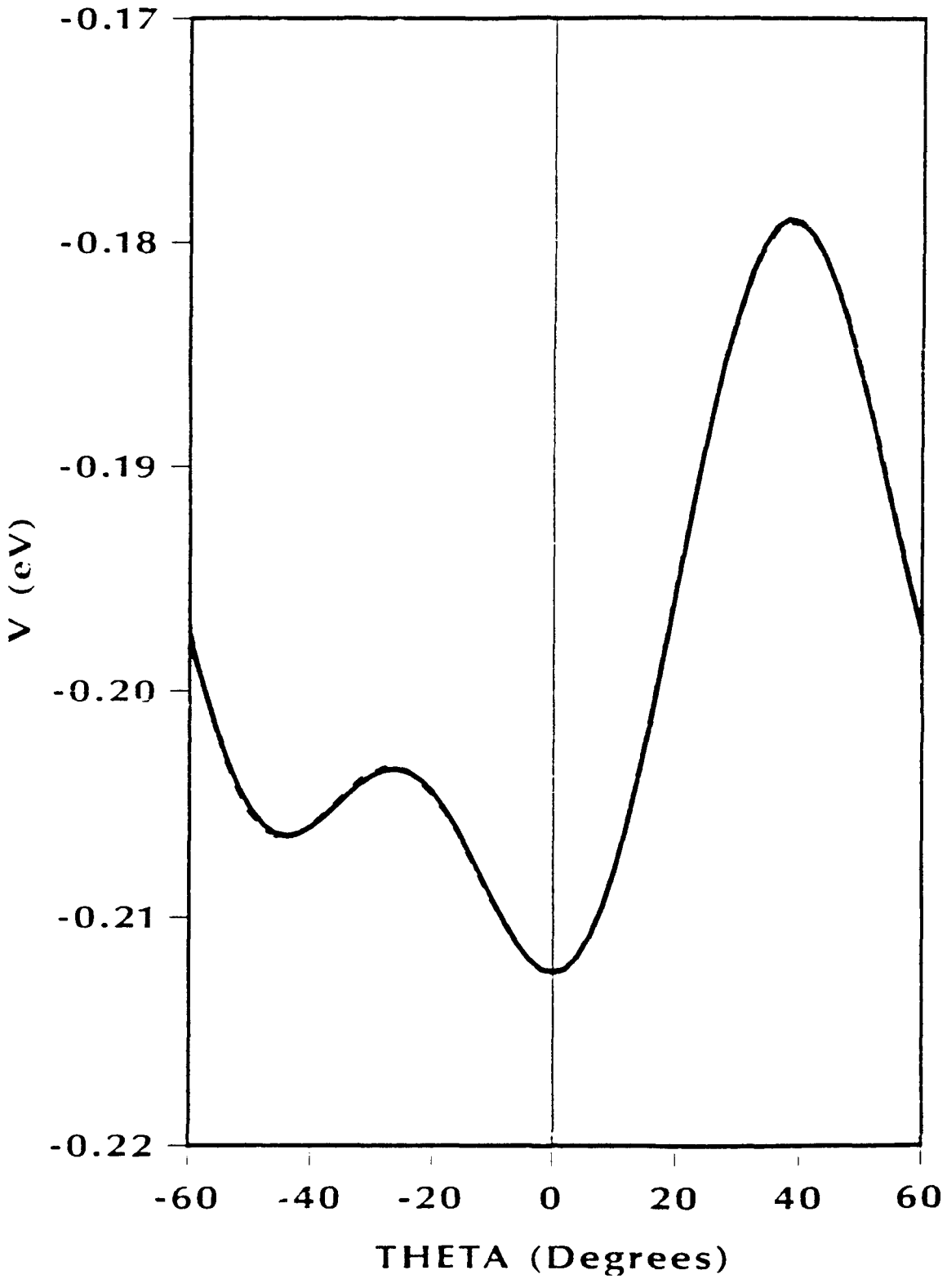

Figure 1. V(θ) as a Function of Methyl Group Orientation About the CN Bond.

Attempts were made to use various standard forms for pairwise interactions (Lennard-Jones, Buckingham, Morse, and modifications of these). The various forms were capable of producing the correct shape of the rotational potential but not the correct equilibrium orientation of the methyl group in that the minimum of the rotational potential was invariably displaced by approximately 20° from the measured orientation at 4.2 K. In light of the failure to accurately describe the spectroscopy and known equilibrium orientation of the methyl group using these standard functions (which all have the same general features), a method was sought by which the experimental observables would dictate the shape of the H-O interaction potential as a function of interatomic distances. A mathematical technique from information theory, the method of maximum entropy (Jaynes 1979), has proven to be capable of attaining the desired result. This method is a technique for computing the "best" distribution of a function (in this case, the potential energy as a function of O-H distance) subject to constraints (the observables). Details of the method and inversion of the experimental data are provided in Rice and Trevino (1991). The result is a potential energy function of novel character and is shown in Figure 2.

The function given is a standard Lennard-Jones function modified by addition of the following two Gaussian functions:

$$V(r) = \varepsilon \{(\sigma/r)^{12} - (\sigma/r)^{6}\} + \Sigma\, a_i \exp(-b_i[r-r_{oi}]^2),$$

where the values of these parameters are provided in the first column of Table 1. The feature at 3.5 Å is absolutely necessary for reproducing the measured spectroscopy and the orientation of the crystal.

A test of the reliability of this function consisted of obtaining the rotational potential V(θ) corresponding to the lattice parameters of the crystal at elevated pressures as measured by Cromer, Ryan, and Schiferl (1985). We found that below 3.5 GPa, the classical barrier height for rotation was approximately room temperature, consistent with a weakly hindered rotor. At 3.5 GPa, the classical barrier height is 18 times that of room temperature, suggesting that the methyl group is firmly fixed in place at this pressure. In addition, the minimum in V(θ) at this pressure occurs at an orientation of 45° with respect to the equilibrium orientation at 4.2 K, ambient pressure, in exact agreement with the conclusions of the x-ray diffraction study (Cromer, Ryan, and Schiferl 1985). We wish to stress that the high pressure crystallographic

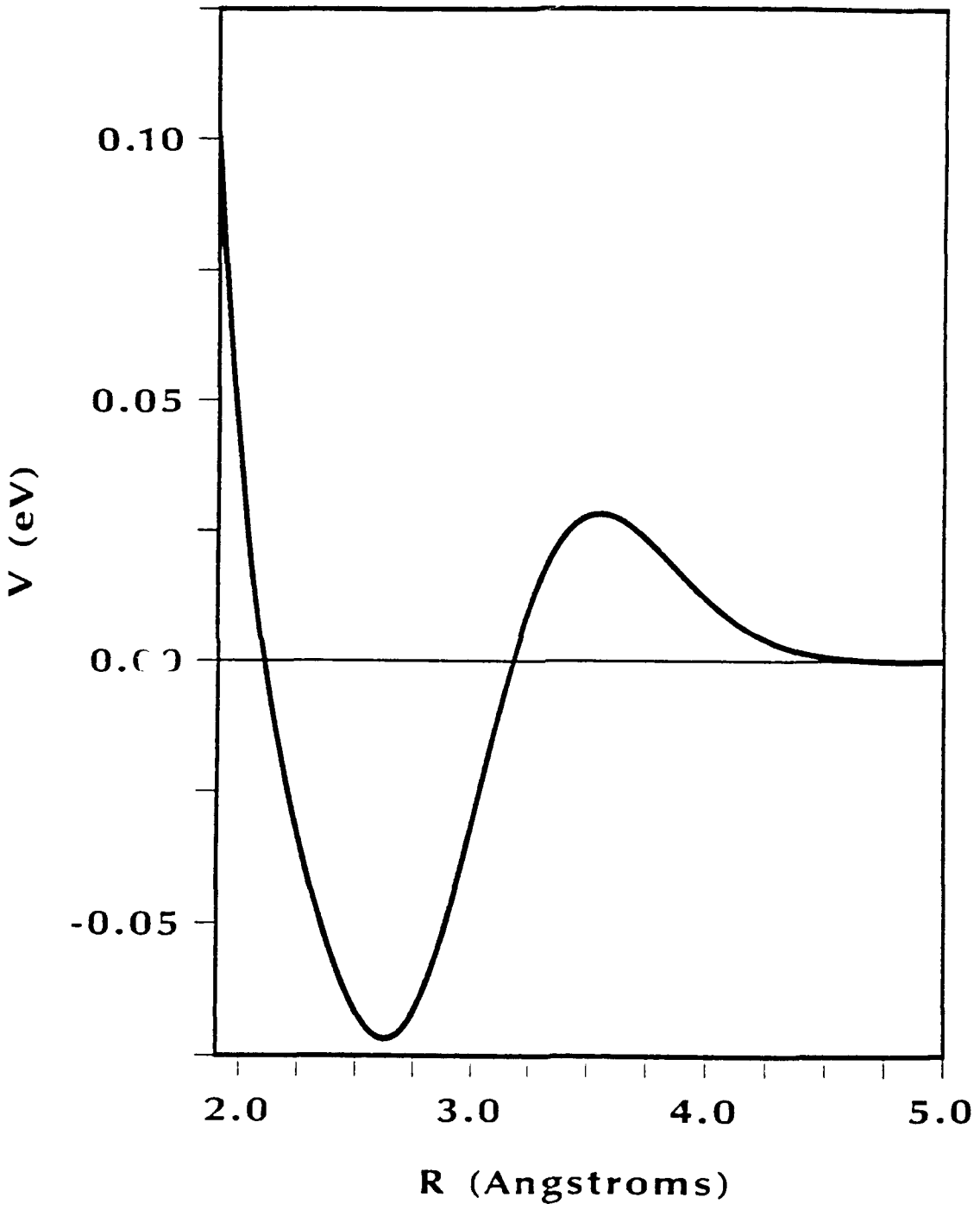

Figure 2. H-O Interaction as Function of Internuclear Distance, Determined From Maximum Entropy Excercise.

Table 1. Potential Energy Parameters

	H-O[9]	H-O	H-H	O-O
ε(eV)	0.012840	0.188238	0.000360	0.007758
σ(Å)	2.337226	2.225917	3.691399	2.788952
a_1(eV)	-0.077142	-0.018822	—	—
b_1(Å^{-2})	3.632857	9.657916	—	—
r_{e1}(Å)	2.683570	2.906931	—	—
a_2(eV)	0.037225	0.018131	—	—
b_2(Å^{-2})	2.818097	1.349721	—	—
r_{e2}(Å)	3.375131	3.442820	—	—

information was not used in the maximum entropy exercise of obtaining the description of the H-O interaction.

This success does not constitute a complete description of all of the intermolecular interactions. At a minimum, the intermolecular H-H and O-O interactions must be provided. In this subsequent effort, in addition to the previous information, we have required that the total intermolecular interactions produce 1 atm internal pressure corresponding to the crystal structure at 4.2 K. The pressure was calculated in the usual manner using the virial expression. The general shape of the H-O interaction was maintained. The H-H and O-O interactions were found to be adequately described by Lennard-Jones potentials. The parameters for these potentials were adjusted using nonlinear least squares in order to fit the previously described experimental data. The pairwise additive potential functions which resulted from this procedure are shown in Figure 3, and the parameters are listed in the last three columns in Table 1.

As a first trial of the assumed interaction potentials, we performed constant NPT Monte Carlo calculations of rigid body nitromethane molecules in which only the lattice constants were allowed to vary. The Monte Carlo model was a box with periodic boundary conditions, the length of which is five crystallographic unit cells on each side. This consists of 500 molecules in the Monte Carlo simulation box. Figure 4 shows the three lattice parameters as a function of temperature. Experimental results are denoted by filled circles, and calculated values are denoted by crosses. The pressure is held constant at 1 atm. Although the

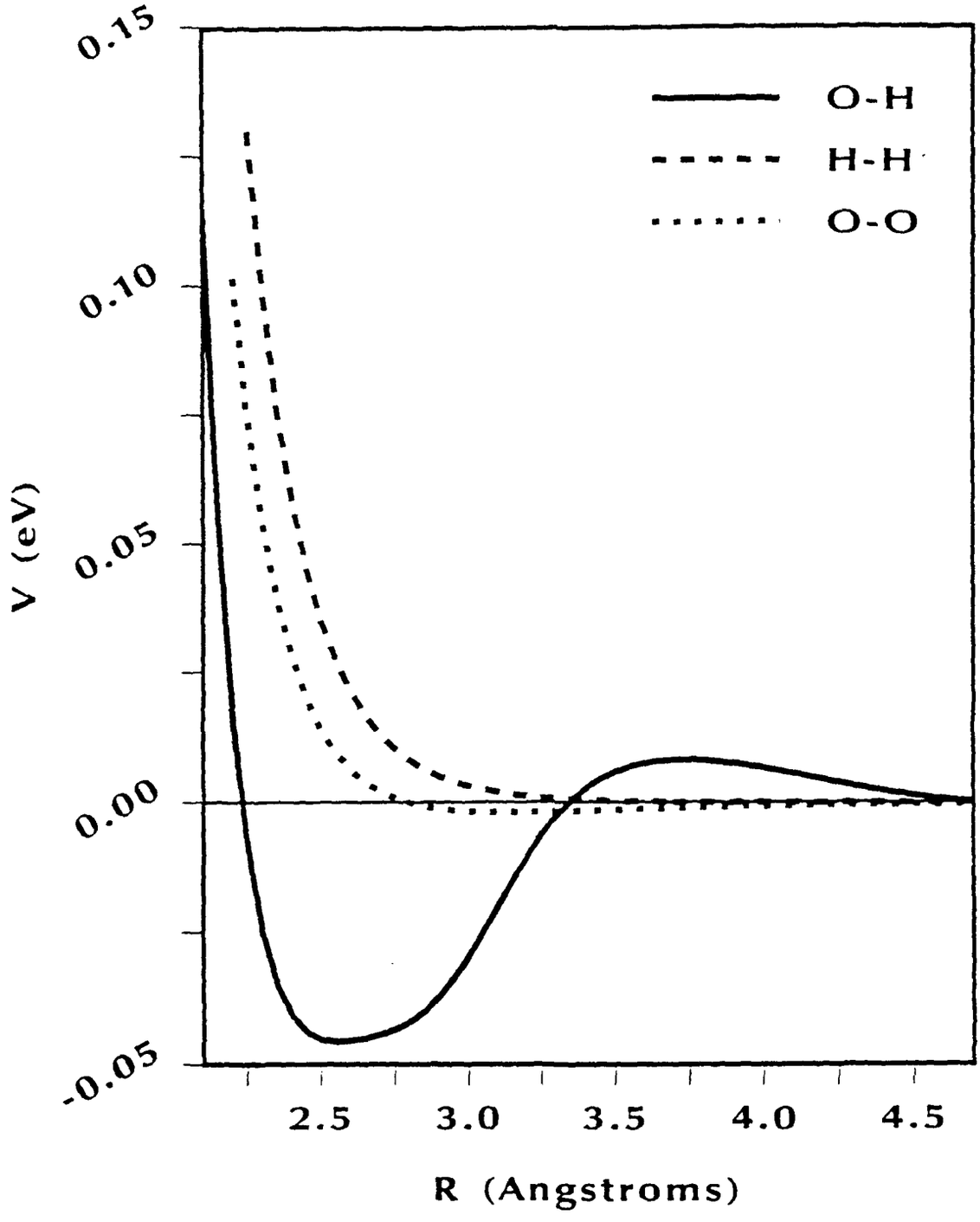

Figure 3. Pair Interaction Potentials as Functions of H-O, H-H, and O-O Internuclear Distances.

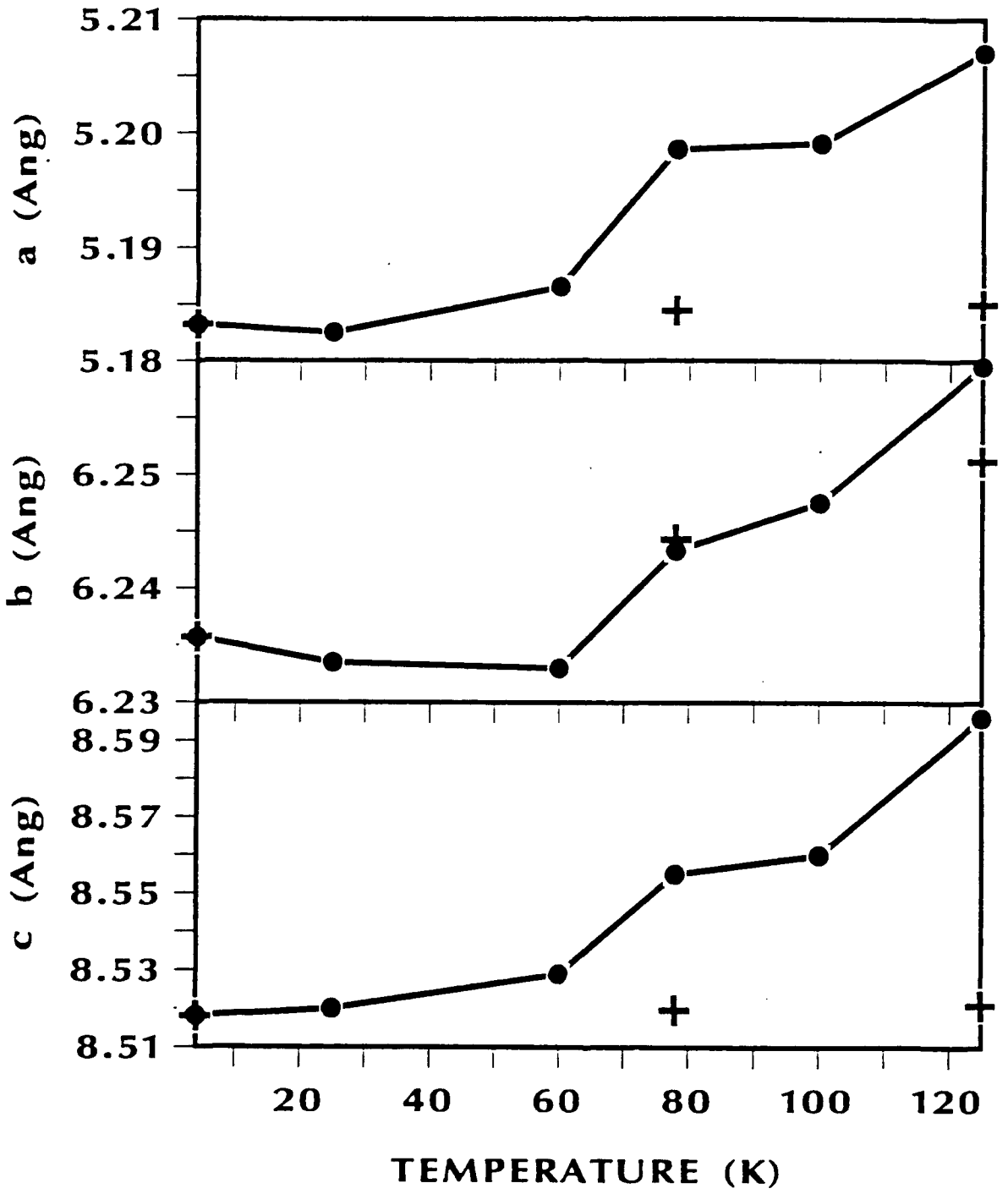

Figure 4. Latice Constants as a Function of Temperature. Pressure is Fixed at 1 atm.

calculated lattice parameter b is in reasonable agreement with experiment, the calculated parameters a and c are significantly smaller than the measured result, indicating that the crystal lattice does not show the correct behavior of expansion with temperature increase, at least within the approximation of disallowing reorientation of the molecules in the unit cell. The variation of the calculated lattice parameters as a function of pressure (denoted by crosses) at a constant temperature of 298 K is shown for comparison with experimentally determined values (denoted by filled circles) in Figure 5. At pressures below 1 GPa, the calculated results are in reasonable agreement with experiment; however, at higher pressures, both lattice parameters a and c do not show the correct compression of the crystal with increasing pressure. The lattice parameter b, however, appears to reproduce the experimental result at all pressures. It is our intention to perform Monte Carlo calculations in which the orientation of the molecules, the center of mass positions of the molecules, and the torsions of the methyl group are allowed to vary as functions of temperature and pressure for those values which are available from experiment. If this model proves consistent with known experimental data, we will use molecular dynamics and Monte Carlo to obtain both time dependent and static properties at temperatures and pressures not easily obtainable by experimental techniques. We hope these results will be useful to the shock wave and detonation communities.

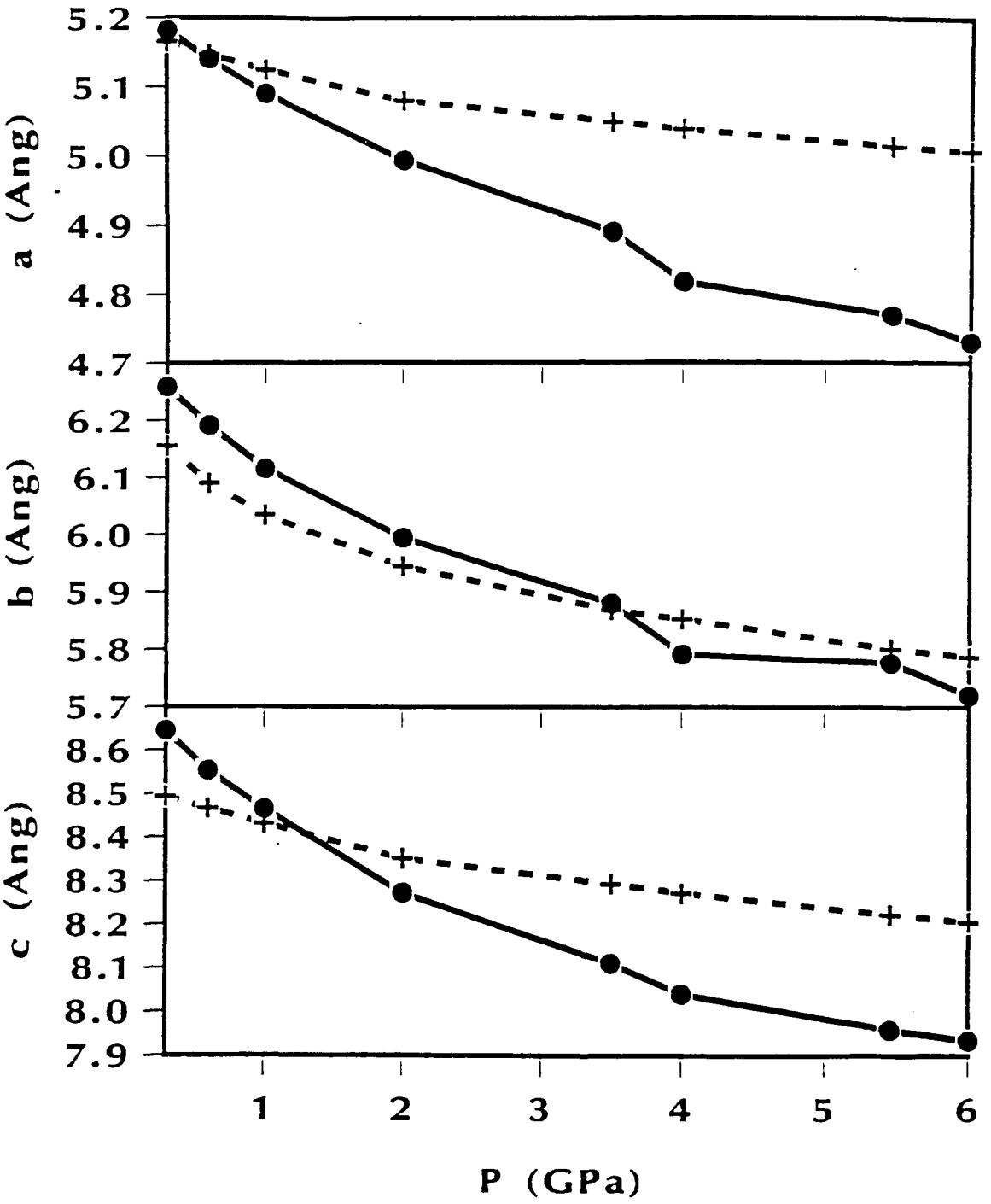

Figure 5. Lattice Constants as a Function of Pressure. Temperature is Fixed at 298 K.

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