

A New Five-Site Pair Potential for Formic Acid in Liquid Simulations

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We propose a new five-site pair potential for formic acid to be employed in liquid state simulations. The pair potential excellently fits to the MP2/6-31G(d) ab initio dimer potential surface, correctly captures the characteristics of the most important regions of the potential, and locates all seven minima found in ab initio calculations. Both thermodynamical quantities and total radial distribution functions for liquid formic acid were computed employing Monte Carlo simulation techniques. We found excellent agreement between experiment and theory with respect to thermodynamics and structure. The results of the total radial distribution functions exhibit significant improvement compared to the results of the OPLS parameter set.

Introduction

Formic acid, the simplest carboxylic acid, is a compound of special interest in many respects. It is, for example, quite puzzling that the gas phase structure of formic acid is completely different from that of the crystalline formic acid; namely, the molecules form predominantly cyclic hydrogen bonding dimers in gas phase,¹ whereas the crystal structure can be characterized by long, catameric chains containing C–H···O hydrogen bonds.² The study of liquid phase formic acid can provide an important link of chain in understanding the physics underlying this observation. The molecular details of the liquid structure can be extracted from direct comparison of liquid simulations and diffraction experiments. One of the most problematic elements of classical liquid simulation procedures concerns the employed potential. The most widely used (and computationally most tractable) potentials compute the intermolecular potential as a combination of a Coulombic interaction term between the point charges situated on the appropriate sites of the molecules and a Lennard-Jones type 6-12 contribution.³ The interaction energy between two molecules is calculated according to eq 1:

$$U_{ij} = \sum_{ij} (q_i q_j / r_{ij} + 4\epsilon_{ij}((\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6)) \quad (1)$$

where site i belongs to the first molecule and j to the second and the summation runs over all sites of the molecules. The point charge associated with site i is denoted by q_i , r_{ij} is the separation between sites i and j , and σ_{ii} and ϵ_{ii} are empirical parameters, whereas σ_{ij} and ϵ_{ij} are calculated as the arithmetic mean and geometrical mean, respectively, of the corresponding parameters. The total energy of the system (U) is calculated as the sum of the pairwise energy contributions.

To the best of our knowledge, there has been no potential developed specifically for formic acid. The only potential employed in formic acid⁴ simulation is based on the optimized potentials for liquid simulations (OPLS) parameter set of Jorgensen and his co-workers originally developed for acetic acid.⁵ The OPLS treats the carbon and the formic hydrogen as a united atom. In recent studies C–H hydrogen bonds were anticipated to be quite important in the crystals of carboxylic acids.⁶ Moreover, in another paper, one of us reported the existence of seven minima (global and local) on the formic acid

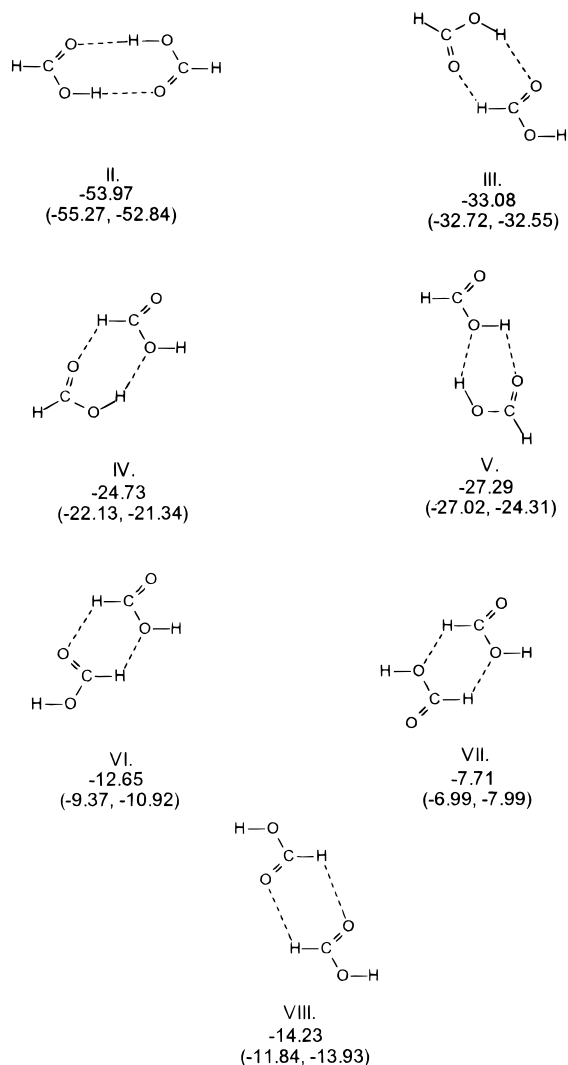


Figure 1. Structures and dimerization energies (in kJ/mol) of seven minima located on the ab initio dimer potential surface.⁷ The first number corresponds to the present parameter set. Numbers in parenthesis indicate MP2/6-31G(d) and MP2/D95++(d,p) interaction energies corrected for BSSE, respectively.

dimer potential hypersurface (see Figure 1, with the numbering of the original paper) which include stable dimers containing

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TABLE 1: Optimized Parameters and Charges of Formic Acid Monomer

i	q_i (e)	σ_{ii} (Å)	ϵ_{ii} (kJ/mol)
C	0.44469	3.727	1.573
(C=)O	-0.43236	2.674	5.079
(C-)O	-0.55296	3.180	1.640
(C-)H	0.10732	0.800	0.084
(O-)H	0.43331	0.994	0.418

C-H...O interactions.⁷ Obviously, a potential employing united CH atom in formic acid cannot be able to model and reproduce fine details of the liquid structure resulting from the possible presence of C-H...O interactions. In the present article, we address the question of developing a five-site pairwise potential for formic acid fit on ab initio potential surface. This all-site approach takes C-H...O interactions explicitly into account in liquid phase simulations. To minimize the possibility and consequences of ill-conditioned parameter estimations, we compare the capabilities of our newly optimized potential to (a) the calculated ab initio potential and (b) experimental structural and thermodynamical data of liquid formic acid. We also illustrate the superiority of our potential over the OPLS set.

Results and Discussion

Ab Initio Calculations. We modeled the dimer potential surface by calculating the potential at a finite number of points in the dimer configurational space at MP2/6-31G(d) level of theory. The MP2/6-31G(d) method, on one hand, involves computation of part of the correlation energy which can be important for hydrogen-bonding complexes, while, on the other hand, it is still reasonable from computational point of view. In this sense, thus, the chosen method proved to be a sensible compromise between accuracy and computational cost. The monomers were treated as rigid objects in their respective geometry taken from the optimized monomer. The starting point of our study was the reliable sampling of the potential surface of the dimer configurational space. The dimer configurations are defined by six intermolecular parameters describing the relative orientation and position of the monomers in the dimer. We generated 536 formic acid dimer configurations by independently varying these parameters. Of all the configurations, 320 are clustered around the four most stable dimer configurations of ref 7 (see dimers II–V in Figure 1). The remaining 216 configurations were selected by distributing the 6 intermolecular degrees of freedom to reasonably sample as many regions of the configurational space as possible. The calculated interaction energies were corrected to basis set superposition error (BSSE) by the functional counterpoise procedure of Boys and Bernardi.⁸ The ab initio calculations were performed using the Gaussian 94 program package.⁹ A simple potential combining a Coulombic interaction and Lennard-Jones type contribution to the interaction energy (see eq 1) was then fit to the ab initio potential surface.

The charges and the optimized parameters located on the atomic sites of the formic acid molecule are collected in Table 1. As mentioned above, the geometric parameters are taken from MP2/6-31G(d) monomer optimization. The bond lengths are 1.213, 1.350, 1.096, and 0.980 Å for C=O, C–O, C–H,

and O–H bonds, respectively. The three parameters defining the bond angles are 125.1°, 125.5°, and 106.1° for $\alpha_{\text{O=C-O}}$, $\alpha_{\text{H-C=O}}$, and $\alpha_{\text{H-O-C}}$ angles. The formic acid monomer is assumed to be planar in our calculations. The charges are based on MP2/6-31G(d) monomer calculation but are slightly adjusted (charges are scaled down by a factor of 0.81 and a small charge of +0.05e are transferred from the C–H hydrogen to the O–H hydrogen) to provide the best possible fit with the ab initio potential surface. The weighted fit of the potential¹⁰ is excellent, resulting in less than 4 kJ/mol root mean square deviation on all configurations. Note that parameters are assigned to *all* five sites of the formic acid molecule in the present model.

To test if the proposed potential set correctly captures the main characteristics of the ab initio potential surface, we attempted to locate all the minima (local and global) on the dimer potential surface suggested in ref 7. Figure 1, in which the appropriate structures and optimized interaction energies calculated with the present parameter set and with MP2/6-31G(d) and MP2/D95++(d,p) method were collected, illustrates that our newly proposed set is able to locate all seven minima of the dimer potential surface and to predict the interaction energies in quite good agreement with not only the MP2/6-31G(d) calculations but also with higher level of theory, as well. The relative energetic order of the various minima is also reproduced correctly. It is noteworthy that the new set excellently locates dimers exclusively containing C–H hydrogen bonds (such as dimers VI–VIII).

Liquid Simulations. We also performed Monte Carlo simulation on the (N,p,T) ensemble with 500 formic acid molecules at 298 K and 10⁵ Pa. In each particle transfer step, a randomly selected molecule was translated in a random direction by a random distance which was no more than 0.3 Å. This displacement was followed by a random rotation of the molecule of less than 10° around a random axis. After every N th particle transfer step, a volume change of the simulation box of no more than 400 Å³ was also performed. The simulation resulted in about 1:2 ratio of the accepted moves to the total trials for the particle transfer steps and in about 1:3 ratio for the volume changing steps. In the simulation, all interactions were truncated to zero at the center–center distance of 15 Å with the C atoms being the molecular centers. To correct for the long-range electrostatic interactions of the molecules, we employed the reaction field correction method with conducting boundary conditions.¹¹ The Lennard-Jones interactions beyond the cutoff distance were taken into account in an average way.³ Initially, we equilibrated the system for 1000N particle transfer steps. The calculated properties were then averaged on 10000 independent equilibrium configurations separated by N particle transfer steps each.

The computed thermodynamic quantities are summarized and compared to the experimental results in Table 2. Clearly, the most important thermodynamic quantities, the potential energy and the density of the liquid, are very well reproduced. The experimental potential energy is obtained from the heat of vaporization of formic acid¹² assuming formic acid to be an ideal gas in the vapor phase. The simulated energy agrees within 1.5% of the experimental value, giving far better agreement with the experiment than that obtained using the OPLS set (46.3 kJ/mol).⁴ The C_p heat capacity, which is the

TABLE 2: Selected Thermodynamic Properties of Liquid Formic Acid

	U (kJ mol ⁻¹)	ρ (g cm ⁻³)	V_{molar} (cm ³)	C_p (J mol ⁻¹ K ⁻¹)	α (10 ⁻⁵ K ⁻¹)	κ_T (10 ⁻¹⁰ Pa ⁻¹)
simulation	39.46 ± 0.29	1.199 ± 0.008	38.40 ± 0.30	102.75	147.4	4.35
experimental	38.96 ^a	1.214 ^b	37.90 ^b	99.04 ^b	102.3 ^c	6.47 ^b

^a Reference 12. ^b Reference 13. ^c Calculated using the data and equations from ref 13, pp 28 and 360.

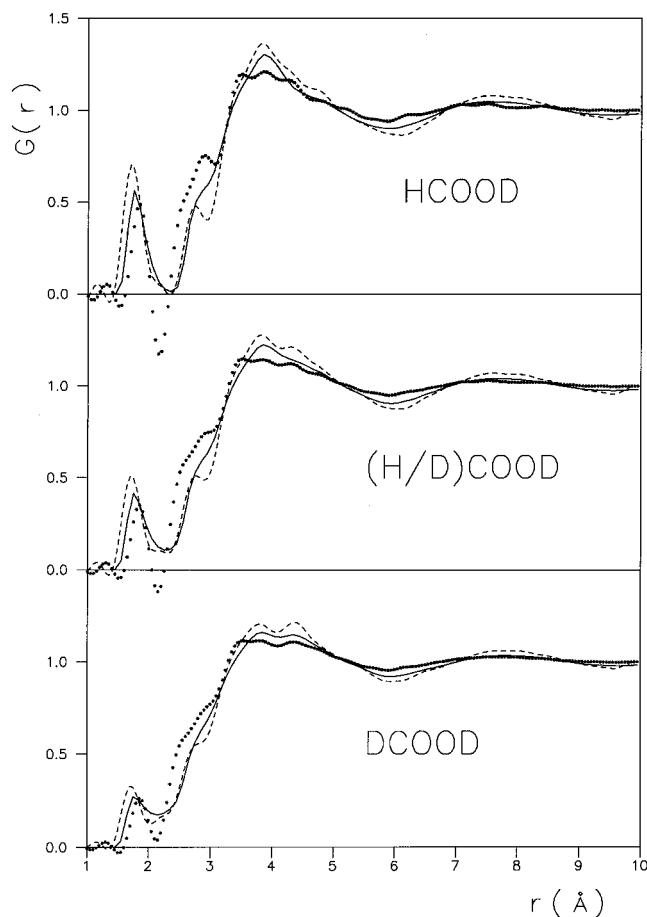


Figure 2. Three total radial distribution functions of liquid formic acid. Solid lines, present simulations, dashed lines, previous simulations with the OPLS potential;⁴ dotted lines, neutron-scattering experiments.¹⁴

sum of the configurational heat capacity computed from the fluctuations of the enthalpy of the system³ and the heat capacity of the ideal gas of formic acid,¹³ also agrees very well (within 3–4%) with the experimental value. The agreement between calculated and experimental thermal expansion coefficients (α) and isothermal compressibilities (κ_T) are also reasonable, considering that both quantities can be calculated from the fluctuations of the volume of the system³ and that the convergence of the latter is extremely slow. Thus, the numerical values of both α and κ_T can only be determined with large inaccuracy.

We also tested the capability of the present potential by comparing three experimental radial distribution functions, $G(r)$, determined by neutron scattering¹⁴ with their simulated counterparts. The three experiments were carried out on formic acid samples deuterated on the acidic hydrogen with different isotopic substitution on the formic hydrogen, namely on DCOOD, on HCOOD, and on a mixture containing 35.9% DCOOD and 64.1% HCOOD in which the average coherent scattering length of the formic hydrogen atoms is zero. This mixture will be referred to as (H/D)COOD. Comparison of the experimental and simulated functions can be seen in Figure 2. Results of a previous simulation⁴ with the OPLS potential are also indicated.

The match of experimental and simulated $G_{\text{DCOOD}}(r)$ is excellent: the hydrogen-bonding peak at about 2 Å, the shoulder of the main peak between 3.5 and 4.5 Å, and the peak assigned to the second coordination shell at about 8 Å are all well reproduced. The fit of the other two functions are less spectacular than that for DCOOD. Nevertheless, the important features of the experimental functions are satisfactorily repro-

duced. The most important deviation is that the amplitudes of the oscillation of the simulated functions beyond the first coordination shell are larger than those of the experimental ones. The difference between experiment and simulation, however, is still considerably smaller than for the corresponding functions obtained by using the OPLS set.⁴ Furthermore, results of recent neutron diffraction experiments suggest that the real amplitudes of these oscillations are probably slightly larger than those of the present experimental curves.¹⁵ Another mismatch occurs between the experimental and calculated functions around the minimum after the hydrogen-bonding peak. This anomaly is probably a consequence of the uncertainty in the experimental data reduction process, namely in the separation of the inter- and intramolecular parts of the radial distribution functions. In the distance range of this minimum of about 2.4–2.8 Å both intra- and intermolecular atom–atom separations can occur in liquid formic acid.¹⁶ The observation that the minimum drops below zero for (H/D)COOD (which, obviously, has no physical meaning) underlines this assumption.

More detailed energetical and structural analysis of the simulations and evaluation and discussion of the consequences of the introduction of the five-site model are under way and will be published in a forthcoming paper.¹⁷

Conclusions

In this study, we proposed a new five-site pair potential for liquid formic acid. The new potential was developed keeping more recent experimental and theoretical observations in mind in order to point to the potentially important role of C–H···O interactions in the liquid phase of *pure* formic acid. We illustrated that the new potential excellently reproduces the main features of the calculated *ab initio* dimer potential surface including correct identification of all (global and local) minima. Liquid simulations on formic acid demonstrated the capabilities of the new potential in reproducing experimental structural and thermodynamics data. Comparison of the results of the present calculations to those of OPLS indicates that the present model can yield more reliable information on liquid formic acid than the OPLS parameter set.

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